



# THE SOCIETY OF RHEOLOGY

## 90<sup>TH</sup> ANNUAL MEETING PROGRAM AND ABSTRACTS

Westin Galleria Houston  
Houston, Texas  
October 14 - 18, 2018

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# Meeting Schedule

## Monday, October 15, 2018

	GLI	PZ1	BL	PO	SF	TG	PZ2
8:30			W. Poon (PL1) - <i>GLI</i>				
9:20			Coffee Break				
9:50	SC1	FC1*	AM1	PS1	ET1	BA1	FP1
10:15	SC2	FC2	AM2	PS2	ET2	BA2	FP2
10:40	SC3	FC3	AM3	PS3	ET3	BA3	FP3
11:05	SC4	FC4		PS4	ET4	BA4	FP4
11:30	SC5	FC5	AM5	PS5	ET5		FP5
11:55			Lunch Break / Student-Industry Forum				
1:30	SC6	FC6	AM6	PS6	ET6	BA6	FP6*
1:55	SC7	FC7	AM7	PS7	ET7	BA7	FP7
2:20	SC8	FC8	AM8	PS8	ET8	BA8	FP8
2:45	SC9	FC9	AM9	PS9	ET9	BA9	FP9
3:10			Coffee Break				
3:45	SC10	FC10	AM10	PS10	ET10*	BA10	FP10
4:10	SC11	FC11	AM11	PS11	ET11	BA11	FP11
4:35	SC12	FC12	AM12	PS12	ET12	BA12	FP12
5:00	SC13	FC13	AM13		ET13	BA13	FP13
5:25			End				
6:30			Monday Evening Reception				

## Tuesday, October 16, 2018

	GLI	PZ1	BL	PO	SF	TG	PZ2
8:30			M. Rubinstein (PL2) - <i>GLI</i>				
9:20			Coffee Break				
9:50	SC14	PM1	AM14*	PS14	DA1	BA14	NF1
10:15	SC15	PM2	AM15	PS15	DA2	BA15	NF2
10:40	SC16	PM3	AM16	PS16	DA3	BA16	NF3
11:05	SC17	PM4	AM17	PS17	DA4	BA17	NF4
11:30	SC18	PM5		PS18	DA5	BA18	NF5
11:55			Lunch Break / Society Business Meeting				
1:30	SC19	PM6	PG1	PS19*	DA6	BA19	NF6
1:55	SC20	PM7	PG2	PS20	DA7	BA20	NF7
2:20	SC21	PM8	PG3	PS21	DA8	BA21	NF8
2:45	SC22	PM9	PG4	PS22		BA22	NF9
3:10			Coffee Break				
3:45	SC23	PM10	PG5	PS23	DA9*	FE1	NF10
4:10	SC24	PM11	PG6	PS24	DA10	FE2	NF11
4:35	SC25	PM12	PG7		DA11	FE3	NF12
5:00	SC26	PM13	PG8			FE4	NF13
5:25			End				
7:00			Awards Reception				
8:00			Awards Banquet				

## Wednesday, October 17, 2018

	GLI	PZ1	BL	PO	SF	TG	PZ2
8:30			L. M. Walker (PL3) - <i>GLI</i>				
9:20			Coffee Break				
9:50	SC27*	PM14	PG9	SG1	ET14	FE5	NF14*
10:15	SC28	PM15	PG10	SG2	ET15	FE6	NF15
10:40	SC29	PM16	PG11	SG3	ET16	FE7	NF16
11:05	SC30	PM17	PG12	SG4	ET17	FE8	NF17
11:30	SC31	PM18	PG13	SG5	ET18	FE9	NF18
11:55			Lunch Break				
1:30	SC32	PM19*	PG14	SG6	ET19	FE10	NF19
1:55	SC33	PM20	PG15	SG7	ET20	FE11	NF20
2:20	SC34	PM21	PG16	SG8	ET21	FE12	NF21
2:45	SC35	PM22	PG17	SG9	ET22	FE13	NF22
3:10			Coffee Break				
3:45	SC36	PM23	PG18*	SG10	ET23	FE14	NF23
4:10	SC37	PM24	PG19	SG11	ET24	FE15	NF24
4:35	SC38	PM25	PG20	SG12	ET25	FE16	NF25
5:00	SC39	PM26		SG13	ET26	FE17	NF26
5:25			End				
6:30			Poster Session & Reception				
6:30			Gallery of Rheology Contest				

## Thursday, October 18, 2018

	GLI	PZ1	BL	PO	SF	TG	PZ2
8:00			T. Divoux (AP1) - <i>GLI</i>				
8:40	SC40	PM27	PG22	SG14*	ET27	FE18	NF27
9:05	SC41	PM28	PG23	SG15	ET28	FE19	NF28
9:30	SC42	PM29	PG24	SG16	ET29	FE20	NF29
9:55			Coffee Break				
10:25	SC43	PM30	PG25	SG17	ET30	FE21	NF30
10:50	SC44	PM31	PG26		ET31	FE22	NF31
11:15	SC45	PM32				FE23	NF32
11:40		PM33					NF33
12:05			End				

## Session and Room Codes

AM = Additive Manufacturing  
 AP = Award Presentations  
 BA = Biological and Active Matters  
 DA = Design of Applied Materials  
 ET = Advanced Experimental Techniques/Methods in Rheology  
 FC = Flow Assurance of Crude Oil & Derivatives  
 FE = Foams, Emulsions & Interfacial Rheology  
 FP = Food, Pharmaceuticals & Cosmetics  
 GR = Gallery of Rheology Contest  
 NF = Non-Newtonian Fluid Mechanics & Flow Instabilities  
 PG = Polyelectrolytes, Self-assembling Systems & Gels  
 PL = Plenary Lectures

PM = Polymer Melts: From Molecular Rheology to Processing  
 PS = Polymers in Solution  
 SC = Suspensions & Colloids  
 SG = Solids, Composites & Granular Materials  
 \* = Keynote

BL = Bellaire  
 GLI = Galleria I  
 PO = Post Oak  
 PZ1 = Plaza I  
 PZ2 = Plaza II  
 SF = San Felipe Room  
 TG = Tanglewood  
 W23 = Woodway II/III  
 WF = Woodway Foyer

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## Monday Morning

### Symposium PL Plenary Lectures

Monday 8:30 Galleria I

PL1

#### **Shear thickening in the real world: The application of suspension rheology to industrial processes**

Wilson Poon

*School of Physics and Astronomy, The University of Edinburgh, Edinburgh, United Kingdom*

Suspensions of non-Brownian particles are ubiquitous in industrial applications. The flow of such suspensions in industrial settings is known to be capricious, being sensitively dependent on a whole range of material parameters and processing conditions; such suspensions often jam in machinery involving complex flow geometries, e.g., extruders. At the same time, mixing liquids into dry powders is of generic importance in many industrial processes. Sometimes, the goal is to generate a flowing suspension; others aim to reduce particle size (wet milling); in yet other applications, the goal is to produce granules (so-called wet granulation). Industrial practitioners typically have difficulty relating shear rheology data obtained in well defined rheometric geometries to any of these applications. I show how recent advances in understanding the shear thickening of high-solid-content granular suspensions can throw light on all of these industrial processes and problems, sketch a unified picture of liquid-powder mixing, wet milling, granulation and extrusion, and propose fruitful avenues for further research in relating fundamental rheology to real-life applications.

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Monday 9:50 Galleria I

SC1

#### **Dynamics of ultrasoft microgels**

Maddalena Mattiello, Sarah Goujard, and Michel Cloitre

*Soft Matter and Chemistry, ESPCI Paris, Paris 75005, France*

Microgels are cross-linked polymeric networks swollen by a good solvent. The particle softness, which is tuned at will by varying the crosslink density, is the key parameter that determines the phase diagram and the rheology of microgel suspensions. Previously, we have identified a scenario where suspensions exhibit well-defined glass and jamming transitions and cross from liquids to entropic glasses and jammed glasses upon increasing the concentration [1]. The rheology of jammed glasses is well described by a micromechanical model where particles interact under the combined action of elastic repulsive forces and viscous drag forces. The flow curves collapse on a generic Herschel-Bulkley equation with an exponent close to 1/2, when the shear rate is scaled by the characteristic time  $\eta/G_0$  ( $\eta$ : viscosity of the suspending fluid;  $G_0$ : low-frequency shear modulus) and the stress by the yield stress [2].

It is not clear whether these results unravel the general behavior of soft microgel suspensions. To address this question, we have synthesized weakly crosslinked microgels. Again the dispersions exhibit a liquid-solid transition, but the glass and jamming transitions can no longer be disentangled. In the dense phase, the suspensions yield above a well-defined strain which does not depend on the concentration. The flow curves still exhibit remarkable scaling properties but the microscopic time  $\eta/G_0$  does not play any role. These results show that the cage deformation is not the key mechanism at the origin of yielding and that the deformation of individual particles needs to be considered. These specificities are reflected into the shear thinning exponent, which is close to 2/3. We propose that ultrasoft microgels belong to a new universality class of soft colloids.

[1] C. Pellet, M. Cloitre, *Soft Matter*, 12, 3710-3720 (2016); [2] J. R. Seth, L. Mohan, C. Locatelli-Champagne, M. Cloitre, R. T. Bonnecaze, *Nature Materials*, 10, 838 (2011).

Monday 10:15 Galleria I

SC2

#### **The hydrodynamics of the colloidal glass transition**

Roseanna N. Zia<sup>1</sup>, Jialun Wang<sup>1</sup>, Gregory B. McKenna<sup>2</sup>, Xiaoguang Peng<sup>2</sup>, and Qi Li<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Stanford University, Stanford, CA, CA 94305-4125, United States*; <sup>2</sup>*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

We study via large-scale Stokesian dynamics simulation the colloidal glass transition and subsequent structural relaxation, utilizing controlled jumps from the liquid state into the putative glass region. We execute such volume-fraction jumps with a range of quench depths and quench rates, where particle size increases at constant system volume. Here we focus on the effects of particle softness as well as lubrication and many-body long-range hydrodynamic interactions on post-jump particle dynamics, where we implement the protocols of the Kovacs signature experiments

(intrinsic isovolume-fraction) to study the approach to a stationary state. The results are compared with light scattering and rheology experiments. The system takes a finite time to reach a metastable intransient state at the widely-accepted colloidal glass transition point, volume fraction 58%, challenging prior assertions that particle dynamics vanish at the glass transition. The exploration of even deeper quenches (higher final volume fractions) up to the random close packing reveals interesting convolution between aging and lag-time dynamics. Detailed study of structural and rheological evolution after the jump are utilized to elucidate the mechanistic process of glassy arrest.

Monday 10:40 Galleria I

SC3

### **Experimental observation of strongly heterogeneous displacements at the depinning transition in a colloidal glass**

Nesrin Senbil<sup>1</sup>, Markus Gruber<sup>2</sup>, Chi Zhang<sup>1</sup>, Matthias Fuchs<sup>2</sup>, and Frank Scheffold<sup>1</sup>

<sup>1</sup>*Department of Physics, University of Fribourg, Fribourg, Switzerland;* <sup>2</sup>*Konstanz University, Konstanz, Germany*

Microscopic observations of probe particles under passive or force driven motion provides unique insights into the dynamics of colloidal dispersions. Here, we study experimentally the motion of polystyrene (PS) probe particles seeded in a micron scale oil-in-water emulsion system. We apply a well-defined constant force on the probe particles via a gradient intensity laser line trap and determine the displacements and probability distributions at various forces in the fluid and glass. Over the range studied, our emulsion droplets acts like hard spheres displaying a jamming and glass transition at 64% and 59% packing fractions, respectively [1]. Both PS particles and emulsion droplets are sterically stabilized and identical in size. The crossover from localized to delocalized behavior happens at a threshold force which highly depends on the composition and corresponding cage strength (in the glass) and cage relaxation (in the fluid) [2]. Our experiments reveal intermittent dynamics and bimodal van Hove distribution functions around a depinning transition at a threshold force. For smaller forces, linear response connects the mean displacement and the quiescent mean squared displacement. We compare our observations to Mode coupling theory (MCT) and find qualitative and semi-quantitative agreement [3].

[1] Zhang C, Gnan N, Mason TG, Zaccarelli E, Scheffold F. Dynamical and structural signatures of the glass transition in emulsions. *J Stat Mech-Theory Exp.* 2016:26. [2] Gruber M, Abade GC, Puertas AM, Fuchs M. Active microrheology in a colloidal glass. *Physical Review E.* 2016;94(4):19. [3] Senbil N, Gruber M, Zhang C, Fuchs M, Scheffold F. Experimental observation of strongly heterogeneous displacements at the depinning transition in a colloidal glass. Submitted. 2018.

Monday 11:05 Galleria I

SC4

### **Microstructure and rheology of associative soft particles glasses**

Fardin Khabaz<sup>1</sup>, Maddalena Mattiello<sup>2</sup>, Michel Cloitre<sup>2</sup>, and Roger T. Bonnecaze<sup>1</sup>

<sup>1</sup>*University of Texas at Austin, Austin, TX, United States;* <sup>2</sup>*ESPCI ParisTech, Paris, France*

Soft particle glasses (SPGs), such as associative microgels, provide a wide range of applications under shear flow due to their tunability of physical properties and unique rheology. In practice, the associative submicron microgels are functionalized with alkyl groups, which are responsible for short-range attractive forces. Therefore in a jammed state, there is a competition between the attractive and repulsive forces. Experimentally it is observed that the strength of the attraction can be tuned with the length of alkyl chains, and in contrast with the repulsive SPGs, these suspensions show flow heterogeneities under shear flow. Here we combine the three-dimensional (3-D) particle-dynamics simulation with the JKR model, which accounts for the attractive forces between the particles, to build a 3-D simulation technique for describing the dynamics of jammed attractive microgels. Simulations tools are used to predict the rheology of these suspensions with different attraction strengths under steady shear flow. At low shear rates, these suspensions exhibit a yield stress and at an intermediate shear rate, the shear stress plateaus for several decades of applied shear rate, which confirms the existence of flow heterogeneities as seen in the experiments. Simulations are used to characterize the origin of the heterogeneities by characterizing the relaxation times corresponding to cage opening and cage association and connect the microstructure and macroscopic properties of attractive microgels.

Monday 11:30 Galleria I

SC5

### **Binary colloidal glasses: Linear viscoelasticity and its link to local structure and dynamics**

George Petekidis<sup>1</sup>, Tatjana Sentjabskaja<sup>2</sup>, Alan R. Jacob<sup>1</sup>, Marco Laurati<sup>3</sup>, Stefan U. Egelhaaf<sup>4</sup>, and Thomas Voigtmann<sup>5</sup>

<sup>1</sup>*IESL, FORTH, Heraklion, Greece;* <sup>2</sup>*Heinrich-Heine University Düsseldorf, Düsseldorf, Germany;* <sup>3</sup>*Universidad de Guanajuato, Leon, Mexico;* <sup>4</sup>*Heinrich-Heine University Düsseldorf, Düsseldorf, Germany;* <sup>5</sup>*Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft und Raumfahrt, Köln, Germany*

We study the fluidization of glass-forming colloidal suspensions due to the presence of a faster small component. We present measurements of the dynamical shear moduli by oscillatory rheology and of the local dynamics by confocal microscopy imaging, for binary colloidal hard-sphere mixtures with large size asymmetry (1 : 5), spanning the whole range of mixture compositions for states close to the glass transition. We compare with Brownian Dynamics simulations and predictions from mode-coupling theory based on the Percus-Yevick approximation to the hard-sphere static structure. Experiments, simulations and theory find a strong decrease of the intermediate-frequency mechanical moduli due to mixing, combined with a fluidization of the system but an increasingly better localization of large particles. We find that the Generalized-Stokes Einstein relation applied to the mean square displacements leads to a reasonable estimate of the shear moduli and indicates that the small particles are mainly responsible for the visco-elastic response of the system.

## Symposium FC

### Flow Assurance of Crude Oil & Derivatives

Organizers: Monica F. Naccache and Rama Venkatesan

Monday 9:50 Plaza I

Keynote FC1

#### **The role of rheology in the O&G flow assurance discipline: Eni's experiences**

Alberto G. Di Lullo

*TA&E, Eni SpA, San Donato Milanese, Milano 20097, Italy*

Flow Assurance is the technical discipline of the O&G Industry dealing with the problems, originated by the behavior of the fluids/solids transported from the reservoir to the receiving facilities, which could prevent the achievement of a cost-effective and safe hydrocarbon production.

In the majority of cases, wells and pipelines transport a mixture of liquid and gaseous hydrocarbons, brine and solids of various nature, both organic and inorganic, mixed at a varying degree. From this point of view, Flow Assurance seems very much related to Rheology.

In Eni, in the last 30 years, many efforts have been made to become proficient in the rheological tools, both from a laboratory point of view and with respect to the rationalization of the observed behavior through mathematical modelling.

Such efforts brought some successes, such as a deeper understanding of ubiquitous Flow Assurance systems (e.g. waxy crudes and hydrates), and of important operations, such as shutdowns and restarts. Nevertheless, the full potential benefit has not been achieved and the role of rheology in the design phase and in the trouble-shooting phase (both covered by Eni head-office) is still minor or niche level. The reasons for this are manifold: the lack of suitable computational tools, the general design approach followed and the difficulty to draw practical conclusions in the production pipelines when some problems occur.

After discussing all the aspects above, we will offer some suggestions as a way forward to turn Rheology into a core discipline for Flow Assurance experts.

Monday 10:15 Plaza I

FC2

#### **Rheology of THF hydrate slurries**

Paulo H. de Lima Silva, Mônica F. Naccache, and Paulo R. de Souza Mendes

*Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, RJ 22451900, Brazil*

Flow assurance is one of the big issues in the oil industry, and hydrates are one of the main causes of pipeline blockage. Rheology provides a means of understanding and optimizing the flow of hydrate slurries in pipelines. Moreover, it can help to investigate new possibilities of additives to mitigate or avoid hydrate formation. In this sense, we analyze the rheology of hydrate slurries formed by a mixture of water and THF (tetrahydrofuran, C<sub>4</sub>H<sub>8</sub>O). THF is miscible in water, and forms hydrates at atmospheric pressure and temperatures above 0 C. Hydrate formation is determined through the use of rheological measurements. We performed a complete rheological characterization of the hydrate slurries formed, for different concentrations of THF. Steady state tests were performed to obtain the flow curve, and the yield stress was determined via creep tests. Thixotropy and elasticity were also evaluated. In addition, we investigated the effect of hydrate inhibitors on the slurry rheology. Three types of alcohol with different concentrations were analyzed. Finally, we present rheological results for hydrate slurries at high pressure and discuss the effect of pressure on the rheology of the systems

Monday 10:40 Plaza I

FC3

#### **Controlled formation and aggregation of hydrate suspensions**

Michela Geri<sup>1</sup>, Krishnaraj Sambath<sup>2</sup>, Ramachandran Venkatesan<sup>2</sup>, and Gareth H. McKinley<sup>1</sup>

*<sup>1</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>Chevron ETC, Houston, TX, United States*

Clathrate hydrates are crystalline cage-like compounds that form when a lattice of hydrogen-bonded water molecules is filled by guest molecules sequestered from an adjacent gas or liquid phase. Understanding hydrate formation and agglomeration is of great importance for flow assurance as hydrate plugs pose a major risk to deepwater production. Being able to easily produce and transport synthetic hydrates is also of great interest given their significant potential as clean energy source and safe option for gas storage. Conventionally, hydrate suspensions are produced from water-in-oil emulsions seeded with few ice/hydrate particles to promote hydrate nucleation&growth. This method often results in long and variable nucleation induction times without guaranteeing conversion of all water droplets. Here we describe a new method to rapidly produce hydrate suspensions at ambient pressure by taking advantage of the Rayleigh-Plateau instability to form a monodisperse stream of droplets during the controlled breakup of a water jet. These small drops are immediately quenched into ice particles via immersion in a deeply subcooled reservoir and can be subsequently converted into hydrates with a dramatic reduction in the induction time. By measuring the evolution of the shear viscosity with time, we monitor the process of hydrate formation for different water volume fractions and imposed shear rates. We show that the observed viscosity increase is initially dominated by a change in effective volume fraction that is independent of both water content and applied deformation rate. We also show that the main mechanism underlying this thixotropic response is related to agglomeration of hydrate particles, which can be controlled and tuned by the addition of surfactants and anti-agglomerants. A theoretical analysis based on an existing model for the rheology of attractive suspensions complements our experimental study in understanding the key mediating role of surfactants and the surprising universality of the agglomeration process.

Monday 11:05 Plaza I

FC4

**The influence of the cooling rate on the yielding of gelled waxy oil**Cezar O. Negrao<sup>1</sup>, Diogo E. Andrade<sup>2</sup>, and Moises A. Marcelino Neto<sup>1</sup><sup>1</sup>DAMEC-PPGEM, UTFPR, Curitiba, Parana 81280-340, Brazil; <sup>2</sup>PPGEM, UTFPR, Curitiba, Parana 81280-340, Brazil

The crude oil at high temperatures in the reservoir loses heat to the surroundings and is submitted to different shear stresses during production and transportation. Thermal and shear histories have great influence on the rheological characteristics of waxy oils at low temperature. Wax crystals precipitate during cooling building up a percolated matrix that entraps the oil and consequently, forming a gel-like structure. One of the main parameters that affect the crystals morphology and consequently the gel strength is the cooling rate. Although the static cooling has been widely studied in the literature many points are not well understood. The current work evaluates the influence of the cooling rate on the gel strength and on the dynamic moduli ( $G'$  and  $G''$ ) of a waxy model oil. Microscopic images of wax crystals obtained for different cooling rates were compared the rheological parameters measured at the same conditions and an explanation for the non-monotonic response of the rheological properties as a function of the cooling rate is proposed based in the crystals morphology.

Monday 11:30 Plaza I

FC5

**Effect of gap thickness on rheological behavior of thin bituminous films**Khushboo Suman<sup>1</sup>, Subhendu Bhattacharya<sup>2</sup>, and Yogesh M. Joshi<sup>1</sup><sup>1</sup>Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India; <sup>2</sup>Shell Technology Centre, Bangalore, Karnataka, India

In this work we investigate the rheological behavior of various grades of bitumen, including that of modified by polymer. This work primarily emphasizes the effect of gap thickness and a variation in the formulation on the linear viscoelastic properties of thin bituminous films. The NMR studies were used to estimate the aromatic to aliphatic ratio of asphaltenes. The tendency of asphaltenes to precipitate increases with increased aromaticity, which could potentially reduce the impact of these asphaltenes on the rheological properties of bitumen. We also carried out the DSC experiments that revealed a presence of multiple glass transitions. We performed the rheological experiments at four different gap thicknesses. Very interestingly, the frequency sweep measurements in a temperature window of 30°C - 90°C successfully lead to validation of time-temperature superposition for all the explored bitumen systems as well as the gap thicknesses. A distinct crossover of elastic modulus over viscous modulus is observed at higher frequency and the timescale associated with the crossover increased with decrease in gap thickness. We attribute such behavior at lower gap thickness to comparable size of asphaltene groups and gap thickness which imparts elastic component to the sample. Furthermore, on conducting creep and recovery tests as per standard protocol, exceptional recovery on removal of applied creep stress in polymer modified bitumen system is observed at all the explored gap thicknesses.

## Symposium AM Additive Manufacturing

Organizers: Anthony Kotula and Patrick Anderson

Monday 9:50 Bellaire

AM1

**Rheology of thermotropic liquid crystalline polymers for generating high-performance strands for use in fused filament fabrication**Mubashir Q. Ansari and Donald G. Baird*Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States*

In this work, dynamic shear rheology was used to select the appropriate thermotropic liquid crystalline polymers (TLCP's) and processing conditions to reinforce polymeric matrices such as acrylonitrile butadiene styrene (ABS) and polyphenylene sulfide (PPS). Due to non-overlapping processing conditions, rheology was used to identify conditions that avoided degradation of the matrix polymers when processed in dual extrusion technology. Small amplitude oscillatory shear (SAOS) tests performed on the available TLCP's in the cooling mode identified the extent of supercooling, which determines if a TLCP has a processing temperature overlap with a polymer matrix. It was found that the extent of supercooling depends on the equilibration temperature from which the TLCP's are cooled from in the SAOS experiments. Because the TLCP melt is unstable below its melting temperature and starts crystallizing, temperatures at which a TLCP are injected into the matrix polymer were determined using SAOS tests in the isothermal mode. These tests were carried out by equilibrating TLCP's above their melting temperature and then cooling to the test temperature. At the test temperature, the crossover of the storage and the loss moduli determined the solidification temperature and time it takes to solidify. Because the TLCP's and the matrix polymers were processed in two different extruders at different temperatures before blending at temperatures below the TLCP melting temperature, processing temperatures in the TLCP-extruders were determined using a shear step strain tests. These tests, performed on the TLCP's, suggested the presence of higher melting crystallites below a certain temperature above the melting temperature, elimination of which is essential to achieve a wider supercooling range of TLCP's. The filaments that were generated exhibited significant improvement in the tensile properties than that of the matrix polymers and were post-processed without melting the TLCP's.



Monday 10:15 Bellaire

AM2

**Modelling polymer melt behaviour during fused filament fabrication**Claire McIlroy<sup>1</sup>, Richard S. Graham<sup>1</sup>, and Peter D. Olmsted<sup>2</sup><sup>1</sup>*School of Mathematical Sciences, University of Nottingham, Nottingham, United Kingdom;* <sup>2</sup>*Department of Physics, Georgetown University, Washington, DC, United States*

The most common method for printing polymer melts is known as fused filament fabrication (FFF), which involves melting a thermoplastic, followed by layer-by-layer extrusion, cooling and re-solidification. The main concern with FFF is weld strength between printed layers; bulk strength is rarely achieved. We use a molecularly-aware, non-isothermal polymer model (Rolie-Poly) to predict how high-shear rates during the deposition process, which involves a 90 degree turn, can stretch and align the polymers with the flow direction [1]. For amorphous melts, we attribute reduced weld strength to a partially disentangled structure at the onset of the glass transition [2]. For semi-crystalline melts, we explore how the stretch induced by the printing flow can enhance nucleation and lead to a gradient in the number of nuclei across a printed layer. [1] McIlroy & Olmsted *J. Rheology* 61 (2017) 379-397 [2] McIlroy & Olmsted *Polymer* 123 (2017) 376-391

Monday 10:40 Bellaire

AM3

**Rheological and heat transfer effects in thermoplastic extrusion additive manufacturing**David D. Phan<sup>1</sup>, Zachary R. Swain<sup>2</sup>, and Michael E. Mackay<sup>3</sup><sup>1</sup>*Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States;* <sup>2</sup>*Department of Materials Science and Engineering, University of Delaware, Newark, DE, United States;* <sup>3</sup>*Materials Science & Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Additive manufacturing, commonly known as 3D printing, provides unlimited design freedom and access to more complex geometries compared to other contemporary manufacturing techniques. Recent advances in this technique have contributed to a diverse palette of printable materials, some of which include: metals, hydrogels, ceramics, and polymers. Complementary to this is a wide variety of printing methods, such as the laser sintering of powders and the controlled extrusion of thermoplastic materials. The latter is often referred to as fused filament fabrication (FFF) or material extrusion (ME) and is the most commercially widespread. In ME, filament of thermoplastic material is conveyed towards a melting zone before being pushed through a computer-controlled nozzle and deposited onto a build plate, with the process being repeated until the desired product is formed. The strength of the final product relies heavily on how well individually laid tracks of molten material “weld” together due to intermolecular diffusion of polymer chains. This diffusion process therefore depends on the temperature the material achieves within the melting zone, making this a heat transfer problem. The complex flow geometry also presents itself as a rheological problem, requiring a unified rheology-heat transfer analysis to understand the ME mechanism. Firstly, we present a modified Cogswell model, which we use to relate extrudate temperatures to entry pressures formed by the flow field. Entry pressure measurements and calculations reveal unintuitive flow behavior, which we believe is attributable to heat transfer limitations within the melt zone. We then present a dimensionless Nusselt-Graetz number analysis using the temperatures obtained from our rheological model and indeed find that heat transfer is a significant bottleneck in manufacturing the strongest printed parts. Future work will focus on applying our models to inform the redesign of ME-based 3D printers.

Monday 11:30 Bellaire

AM5

**Molecular weight dependence of weld formation in material extrusion additive manufacturing**Jonathan E. Seppala<sup>1</sup> and Kalman Migler<sup>2</sup><sup>1</sup>*Materials science and engineering division, National institute of standards and Technology, Gaithersburg, MD 20899, United States;* <sup>2</sup>*Polymer, NIST, Gaithersburg, MD 20899, United States*

Material extrusion (ME) additive manufacturing, after several decades of development, is now an established production method for small volume or highly complicated parts. While ME has transitioned from prototyping to end use production, little is known about the mechanisms that dominate strength development between layers. Previously we reported on a framework for determining weld time and weld strength of ME processed welds, comparing those results to traditional polymer-polymer weld formation. Here we extend that work by systematically varying the weight average molecular weight ( $M_w$ ) of entangled bisphenol-A-polycarbonate ME filaments and measuring weld time and weld strength. The resulting weld formation will be discussed in the context of traditional polymer-polymer welding and weld thickness (inter-penetration depth) during the unique shear and thermal history produced by the ME process.

## Symposium PS Polymers in Solution

Organizers: Nicolas J. Alvarez and Cari Dutcher

Monday 9:50 Post Oak

PS1

### **Rheological scaling of polymerized ionic liquids: From salt-free to ion condensed solutions**

Atsushi Matsumoto<sup>1</sup>, Francesco D. Giudice<sup>2</sup>, Rachapun Rotrattanadumrong<sup>1</sup>, and Amy Q. Shen<sup>1</sup>

<sup>1</sup>Okinawa Institute of Science and Technology Graduate Unvers, Onna, Japan; <sup>2</sup>Swansea University, Swansea, United Kingdom

Polymerized ionic liquids (PILs) are a special type of polyelectrolytes (PELs) with ionic liquid (IL) moieties covalently attached to a polymer backbone. PILs are considered as an ideal class of solid-state polymer electrolytes due to the suppressed electrostatic interaction (sEI) resulting from the sterically hindered and charge delocalized ions. The effect of EI on the rheological properties of PELs in semidilute regimes has been well established [1]. How the sEI effects the rheological properties of PILs is not well understood. To answer this question, we use a model system consisting of a PIL (PC4-TFSI: the poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide)) in a mixture of an IL (BmimTFSI) and a non-ionic solvent (DMF). The BmimTFSI acts as both a solvent and a source of salt ions to regulate the charge screening with the sEI. The specific viscosity ( $\eta_{sp}$ ) and relaxation time ( $\lambda$ ) of PC4-TFSI solutions in the semidilute unentangled regime were measured by using a combination of conventional rheometry and microfluidic rheometry, while varying the concentration of BmimTFSI up to 3.42 M at which the solvent consists of only BmimTFSI molecules. Values of  $\lambda$  agree well with those obtained using dynamic light scattering. We show: when  $10^{-5} \text{ M} < c_{\text{BmimTFSI}} < 0.1 \text{ M}$ , both  $\eta_{sp}$  and  $\lambda$  are initially constants at low  $c_{\text{BmimTFSI}}$  but decrease with increasing  $c_{\text{BmimTFSI}}$ , consistent with the prediction by Dobrynin et al. [1] for PEL solutions. In the range of  $0.1 \text{ M} < c_{\text{BmimTFSI}} < 1 \text{ M}$ , both  $\eta_{sp}$  and  $\lambda$  gradually decrease with increasing  $c_{\text{BmimTFSI}}$ , and display deviations from the theoretical predictions [1]. When  $1 \text{ M} < c_{\text{BmimTFSI}} < 3.42 \text{ M}$ , both  $\eta_{sp}$  and  $\lambda$  increase with increasing  $c_{\text{BmimTFSI}}$ . Our results indicate that the relatively large and charge delocalized ions affect the screening of charges on PILs, consequently influence the rheological behavior of PILs.

[1] Dobrynin, et al., *Macromolecules*, 1995

Monday 10:15 Post Oak

PS2

### **Universal scaling and the characterisation of gelation in associative polymer solutions**

Aritra Santra and Ravi Prakash

*Chemical Engineering, Monash University, Melbourne, Victoria 3800, Australia*

A salient feature of associative polymer solutions is the formation of a reversible gel. The onset of gelation is governed by the polymer concentration, the solution temperature, the number of stickers per chain, and the strength of association between the stickers. Depending on the solution temperature, associative polymer solutions undergo a phase transition and get separated into a sol phase (with finite size clusters) and a gel phase (with system spanning infinite size clusters). Several different hypothesis and theories have been proposed in the literature to characterise gelation in associative polymer solutions, but many issues remain unresolved. In particular, Flory and Stockmayer independently proposed two different models to characterise the post-gel regime, based on differing hypotheses of cluster dynamics. Ishida and Tanaka subsequently developed a framework based on lattice theory to explore the consequences of these differing pictures. They showed that the number average chain-cluster size in the sol phase goes through a maximum at the gelation concentration in Flory's model, while it remains constant in Stockmayer's model, subsequent to the onset of gelation. Using an argument based on mean field theory, Rubinstein and Semenov obtain predicts in line with Flory's model. The concentration at the inception of gelation is currently unclear, and is generally believed to occur approximately at the monomer overlap concentration  $c^*$ . In this work, we carry out multi-particle Brownian dynamics simulations of multi-sticker associative polymer solutions to unambiguously identify the gel-point and we resolve disparities between the different post-gel models. We also verify the universality of scaling relations amongst the various parameters that characterise associative polymer solutions, derived by Rubinstein and Semenov, in both theta and good solvents. Simulation predictions of the zero-shear rate viscosity in the pre- and post-gel regimes are compared with previous theories and observations.

Monday 10:40 Post Oak

PS3

### **Elasto-capillary flow of dilute solutions of associative polymers**

Eugene Pashkovski, Reid Patterson, and David Nickerson

*The Lubrizol Corporation, Wickliffe, OH 44092, United States*

The uniaxial extensional viscosity is a fundamental material property of viscoelastic fluids. The extensional flow can be realized in a Capillary Breakup Extensional Rheometer equipped with a high-speed camera for observing the capillary thinning and breakup of a fluid within several milliseconds. For dilute polymer solutions, the elastocapillary (EC) flow occurs when the polymer concentration is sufficiently high for balancing polymeric elastic stress with the capillary pressure. The lowest polymer concentration  $c_{low}$  for EC flow to be detected decreases with molecular weight (L. Campo-Deaño and Ch. Clasen, *J. Non-Newtonian Fluid Mech.*, 2010, **165**, 1688). As a result, the EC balance can be easily achieved for polymers with very high molecular weight ( $M_w > 10^6$ ) even when  $c_{low}$  is significantly lower than the critical overlap concentration of polymer coils,  $c_{low} \sim 0.01c^*$ . For the non-associative polymers with  $M_w \sim 10^5$ , the EC flow is observed at sufficiently higher concentrations,  $c_{low} \sim 0.1c^*$ . However, when these relatively short chains contain a small fraction of functional groups capable of forming transient interactions, the value of  $c_{low}$  decreases dramatically. Assuming that for  $c_{low} \ll c^*$  the inter-chain associations do not contribute to polymer dynamics, we employ FENE

dumbbell model adopted for EC flow by C. E. Wagner et al. (*J. Non-Newtonian Fluid Mech.*, 2015, **218**, 53) for the analysis of the experimental data.

Monday 11:05 Post Oak

PS4

### **Intermolecular association in the in-situ formed physically cross-linked poly(vinyl alcohol) cryogels**

Nidhi Joshi and Yogesh M. Joshi

*Chemical Engineering, Indian Institute of Technology, Kanpur, Kanpur, India*

Polymer hydrogel are three dimensional polymeric networks capable of imbibing a large amount of water or biological fluids. The biocompatibility, processing ease and mechanical properties of freeze-thaw poly (vinyl alcohol) based hydrogel have encouraged significant research towards developing the materials for various biomedical applications. Poly(vinyl alcohol) cryogels are formed as a result of the freezing of the concentrated solution, storage in frozen state and subsequent thawing. In these cryogels, the linkages of three-dimensional network of polymer chains are formed through non-covalent interactions. Temperature induced evolution of viscoelasticity during gelation of semi-dilute poly (vinyl alcohol) (PVA) in aqueous dispersions was studied through rheological measurements in the linear domain. The work primarily focuses on the effect of number of freeze/thaw cycle, concentration and molecular weight on the inter-structural properties of the PVA cryogels. The critical gel temperature determined by measuring the loss tangent at different temperature and oscillation frequency during freezing and thawing process was found to increase with concentration and molecular weight of the poly (vinyl alcohol). The critical exponent and gel strength value for high molecular weight PVA obtained in the freeze-thaw process was ascribed to the high mechanical strength gel with strong cross-links. The quantitative study verified that high concentration and molecular weight facilitated the PVA chains to undergo association via physical cross-linking and subsequently formed the three dimensional network. The evolution of microstructure in PVA was attributed to the formation of physical knots during the thawing process and evaluated as a function of the number of freeze-thaw cycles, and rate of change of temperature. The structural evolution of porous network in PVA was controlled at first cycle of freeze-thaw method as the change in critical gel temperature was invariant for further number of cycles.

Monday 11:30 Post Oak

PS5

### **Transport of interacting nanoparticles in complex polymeric solutions**

Ryan Poling-Skutvik, Ali Slim, Ramanan Krishnamoorti, and Jacinta C. Conrad

*Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States*

Transport of nanoparticles through complex fluids is essential for environment remediation, nanocomposite processing, and targeted drug delivery. Because nanoparticles are of comparable size to the heterogeneities present in many complex fluids, their dynamics cannot be described through the framework of microrheology but rather decouple from the bulk fluid properties. Indeed, nanoparticles can transport many orders of magnitude faster than expected when coupled to complex fluid relaxations on similar length scales, or much more slowly than expected when physically obstructed. Interactions between the nanoparticles, arising from high particle densities and/or chemical surface modifications, can further modify their transport properties. To understand the underlying physics of transport in this size regime, we measure the dynamics of surface-modified silica nanoparticles moving through polymer solutions, which serve as model complex fluids with well-controlled and tunable heterogeneities, using x-ray photon correlation spectroscopy. Electrostatic charges lead to long-range interactions between the particles in organic solvents without disrupting the structure or dynamics of the surrounding polymer solution. The long-range interparticle interactions slow nanoparticle dynamics across the interparticle distance, even though the nanoparticle dynamics are subdiffusive and coupled to the polymer relaxations. Grafted polymers help to stabilize the nanoparticles in complex fluids and lead to soft physical interactions between the grafted particles and the surrounding polymer chains, with implications for their transport behavior. Our work illustrates that modifying the particle surface chemistry grants excellent control over the transport properties of nanoparticles through complex media.

## **Symposium ET**

### **Advanced Experimental Techniques/Methods in Rheology**

Organizers: Kalman Migler and Simon Rogers

Monday 9:50 San Felipe Room

ET1

### **Using rheo-microscopy to directly correlate structural and mechanical aging in a thermoreversible colloidal gel**

Tuan Nguyen and Matthew E. Helgeson

*University of California, Santa Barbara, Santa Barbara, CA, United States*

Colloidal gels at moderate volume fraction coarsen and age through a complex coupling of kinetic processes including aggregation, phase separation and glass-like arrest, significantly influencing their final structure and mechanical properties. Understanding this coupling is necessary for rheological design, yet requires advanced methods for simultaneous structural and mechanical characterization. Here, we utilize rheo-microscopy on a well-characterized colloidal system with thermoreversible attractions to understand how thermal quenching influences the development of colloidal gel structure and rheology through the coupling of gelation and arrested phase separation. Synchronized linear viscoelastic measurements and bright-field optical microscopy, along with custom image analysis, resolve morphological and structural features of phase separation at length scales much larger than individual colloids. The results provide a unique window into the relationship between rheological aging and coarsening of large-scale structure. For example, we find that varying the quench rate and depth provides control over the relative kinetic time scales for gelation and arrest. Time-resolved texture analysis microscopy reveals a linear growth rate in the dominant length

scale of phase separation that is consistent with late-stage spinodal decomposition. Differential dynamic microscopy analysis reveals mechanisms by which the coarsening occurs, namely the intermittent storage and release of elastic stresses driven by the advection of phase separation. Finally, directly comparing the structural and rheological data provides new insight into the features of gel rheology that are dominated by large-scale structure as opposed to more local measures. Overall, these observations improve our understanding of thermally processed colloidal gels and demonstrate the utility of rheo-microscopy for characterizing kinetic processes in arrested fluids.

Monday 10:15 San Felipe Room

ET2

### **Applications of a new shear-induced polarized light imaging (SIPLI) technique**

Joerg Laeuger and Loredana Voelker-Pop

*Anton Paar Germany, Ostfildern, Germany*

Rheological methods reveal information on macroscopic material properties. However, the mechanical material properties are strongly dependent on the underlying microstructure. Therefore information on the microstructure is often valuable for a better understanding of the rheological behavior. Simultaneous use of rheological and optical techniques, i.e. of rheo-optical methods, is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. Different optical methods such as small angle light scattering, microscopy (polarized, fluorescence, confocal), spectroscopy (NIR, IR, Raman), birefringence and dichroism, as well as pure visualization techniques have been employed. In this paper, applications of a new rheo polarized imaging techniques will be discussed [1]. SIPLI (shear induced polarization light imaging) combines a visualization technique with measurements of local stresses through the detection of the birefringence. By employing parallel-plate geometries, different shear rates are existing throughout the sample, from a maximum shear rate at edge of the sample to a zero shear rate in the center of the plate. With SIPLI the whole plate is observed and the birefringence can be displayed over the full range of shear rates within one single experiment. Applications of the method are presented including simultaneous SIPLI and the rheology of the oriented lamellar phase of block copolymers, liquid crystals, cellulose and block copolymer solutions, as well as a study of the thermally-induced reversible transformation of worm-like micelles to spherical micelles. In addition, a direct relation between the shish formation and the polymer melt viscosity upturn during flow-induced crystallization of semi-crystalline polymers is demonstrated.

[1] O. O. Mykhaylyk, N. J. Warren, A. J. Parnell, G. Pfeifer, J. Laeuger *Journal of Polymer Science, Part B: Polymer Physics*, 54, 2151-2170, (2016)

Monday 10:40 San Felipe Room

ET3

### **Digital holographic rheology of complex fluids**

Siddhartha Gupta and Siva A. Vanapalli

*Texas Tech University, Lubbock, TX, United States*

Mapping the three-dimensional (3D) velocity fields of complex fluids is critical for characterizing fluid rheology, elastic instabilities, particle migration, and slip and shear-banding. Current techniques such as confocal microscopy interrogate the 3D flow volume by depth-wise mechanical scanning which has limitations on rates of image acquisition and mapping unsteady flows. Alternatively, stereoscopic imaging with multiple cameras is used to determine flow fields in 3D, but the depth of focus is limited. Digital holography microscopy (DHM) with particle tracking velocimetry (PTV) is an interferometry approach capable of volumetric imaging by recording holograms of the flow. Therefore, DHM-PTV has the potential to map complex flows but its capabilities have not been fully exploited for probing the kinematics and rheology of complex fluids. Here we use DHM PTV to investigate Newtonian as well as viscoelastic fluid flows in microchannels. We map the full 3D velocity profiles for these fluids which are in good agreement with CFD simulations. We also generate steady shear viscosity curves based on the Cauchy momentum balance equation without invoking any constitutive relation. Our holographic rheology method enables measurement of shear viscosity across three orders of magnitude in shear rate that are in good agreement with macrorheometry. Additionally, we observe wall slip in our experiments with viscoelastic polymer solutions, however, our holographic rheology method is unaffected by wall slip due to our ability to determine locally the relationship between stress and strain rate. In sum, we show DHM PTV enables rapid and accurate analysis of nonlinear rheology of complex fluids and provides a pathway to visualize the structure of complex viscoelastic flows.

Monday 11:05 San Felipe Room

ET4

### **A simple shear cell for direct microstructural characterization of step-stress deformation in soft materials**

Chan K. Hubert<sup>1</sup>, Bharath Rajaram<sup>2</sup>, and Ali Mohraz<sup>3</sup>

<sup>1</sup>*The Clorox Company, Irvine, CA, United States*; <sup>2</sup>*TA Instruments, New Castle, DE, United States*; <sup>3</sup>*UC Irvine, Irvine, CA, United States*

The application of external stresses to a viscoelastic material can induce complex rheological responses such as creep, shear-induced strengthening, and delayed yielding. Understanding the underlying physics of these phenomena requires the ability to characterize how the material's microstructure evolves in response to the externally applied stresses. Here, we introduce a custom-built stress-controlled shear cell coupled to a fast-scanning confocal microscope for direct visualization of constant-stress shear deformation in complex fluids. The torque generator is a cylindrical Taylor-Couette system with a Newtonian fluid between a rotating inner bob and a free-to-move outer cup. A spindle/cone assembly is coaxially coupled to the cup, and transfers the torque exerted by the fluid to the sample of interest in a cone-and-plate geometry. We model and experimentally demonstrate the performance of our device in both steady state and transient experiments with different viscoelastic materials. Our apparatus can accurately conduct unidirectional constant-stress experiments, with the capability to directly visualize the flow field. Importantly, our step-stress experiments on viscoelastic materials are devoid of creep ringing, which is an advantageous aspect of the viscous coupling between

the torque generator and the viscoelastic sample. We specifically demonstrate this aspect of our shear cell both theoretically and experimentally with a rubber-like crosslinked polymer whose viscoelasticity is well approximated by the Kelvin-Voigt model.

Monday 11:30 San Felipe Room

ET5

### **High speed confocal microscopy of sheared colloidal gels**

Gabriele Colombo and Jan Vermant

*Department of Materials, ETH Zürich, Zürich, Switzerland*

Colloidal gels represent an interesting family of soft materials. Despite the wide range of possible technological applications, the microstructural details underlying their typical solid-to-liquid transitions upon shear remain poorly understood. The rheology of colloidal gels is very sensitive to the applied flow history and typically shows a complex behavior including a yield stress and thixotropy. Dramatic changes in mechanical properties may well result from subtle, highly localized microstructural changes, which are difficult to resolve using ensemble averaged techniques as e.g. light scattering. In this work, we intend to evaluate the microstructural basis of thixotropy, by directly imaging colloidal gels under shear. The experimental approach relies on the quantitative study of the gel microstructure using high-speed, structured illumination confocal microscopy. Experiments are performed using a rheometer with a home-made shear cell for counter-rotation of the lower glass plate, allowing single particles to be imaged for long times at the stagnation plane. The stress is directly measured, so that the link between microscopic observations and nonlinear rheology can be established. The unprecedented combination of temporal and spatial resolution of our setup allows the study of intermediate volume fraction gels at high shear rates and with larger than usual fields of view, a critical factor to resolve the large length scales of structural heterogeneity developing in these systems. At low shear rates, a transient network develops with increasingly heterogeneous structure, due to local compaction and the formation of large voids. As shear is increased, structural breakdown takes place and the sample is progressively fluidized. For a model depletion colloidal gel, these transitions are followed quantitatively by real space analysis through both local and large scale descriptors, including the pair correlation function, coordination number distributions and number density variations.

## **Symposium BA Biological and Active Matters**

Organizers: Pushkar Lele and Kelly Schulz

Monday 9:50 Tanglewood

BA1

### **High throughput microfluidic characterization of cell rheology**

Shamim M. Ahmmad<sup>1</sup> and Siva A. Vanapalli<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>2</sup>*Texas Tech University, Lubbock, TX, United States*

Recent advances in microfluidics have led to high throughput rheological characterization of thousands of individual cells. These techniques apply stress to the cells by physically squeezing them through constricted microchannels or by exposing them to shear and extensional flows in unconstricted microchannels at millisecond timescales. The deformed shape of the cells is quantified as a measure of strain. Power law rheology is used to model the whole cell response and rheological properties such as compliance and fluidity are calculated. However, the millisecond time scales at which these techniques operate do not capture cellular mechanics at physiologically relevant timescales of seconds or minutes. In these study, we report a microfluidic analog of micropipette aspirator to probe hundreds of cells at physiologically relevant time scales. In this novel device, cells are parked at prescribed locations and nearly equal hydrodynamic stress is applied to aspirate cells following the principles of micropipette aspiration technique. The equilibrium aspiration length and size of the cell portion outside the aspiration channel is measured as a function of imposed stress to identify the linear regime of deformation. For the chosen cancer cell lines, we find that the deformation data fits better with the elastic solid, allowing us to calculate cellular rheological properties like cortical tension and Young's modulus. We used drugs blebbistatin and paclitaxel to alter the rheological properties of cancer cells and find that our technique is sensitive to these alterations.

Monday 10:15 Tanglewood

BA2

### **Rheological characterization of dynamic re-engineering of the pericellular region by human mesenchymal stem cell-secreted enzymes**

Maryam Daviran, Sarah M. Longwill, Jonah F. Casella, and Kelly Schultz

*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States*

Human mesenchymal stem cells (hMSCs) play an important role in wound healing. They are recruited to injured sites by chemical cues to regulate inflammation and coordinate tissue regeneration. Migration of hMSCs requires invasion of the extracellular matrix (ECM) by secreting matrix metalloproteinases (MMPs) to create migration pathways. Cell-ECM interactions are complex due to inherent environmental physical and chemical cues. To minimize this complexity, we encapsulate hMSCs in a well-defined cell-degradable hydrogel, which mimics aspects of the native ECM. Our hydrogel consists of 4-arm star poly(ethylene glycol) end functionalized with norbornene cross-linked with an MMP degradable peptide sequence. Multiple particle tracking (MPT) microrheology is used to characterize spatial and temporal rheological changes in the pericellular region. In MPT, Brownian motion of fluorescent probes embedded in the material is measured. Previous work measuring hMSC-mediated degradation determined that around the cell the scaffold is not degraded and the cross-link density decreases as distance from the cell increases. This profile suggests that cells are inhibiting degradation around them to enable spreading prior to motility by secreting tissue inhibitors

of metalloproteinase (TIMP), which bind to MMPs and inhibit their activity. hMSCs secrete two TIMPs. We inhibit TIMPs simultaneously and individually to characterize their role in matrix degradation. When both TIMPs are inhibited the degradation profile inverts and is a reaction-diffusion type profile, where the greatest degradation occurs around the cell. In single TIMP inhibition, we measure both types of degradation profiles. We also measure an increase in cell motility. All of the TIMP inhibited data fits well with Michaelis-Menten enzymatic degradation model, with an order of magnitude decrease in the  $k^*$  value when a single TIMP is inhibited. With this simple treatment we have enhanced cell speed in the scaffold, which could increase cell delivery to wounds.

Monday 10:40 Tanglewood

BA3

### Measurement of strength and viscoelasticity of mammalian tissues by dynamic oscillatory rheology

Ria D. Corder<sup>1</sup>, Robert B. Vachieri<sup>2</sup>, Darlene K. Taylor<sup>2</sup>, Jodie M. Fleming<sup>3</sup>, Friederike L. Jayes<sup>4</sup>, and Saad A. Khan<sup>1</sup>

<sup>1</sup>Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States; <sup>2</sup>Chemistry and Biochemistry, North Carolina Central University, Durham, NC 27707, United States; <sup>3</sup>Biological & Biomedical Sciences, North Carolina Central University, Durham, NC 27707, United States; <sup>4</sup>Obstetrics and Gynecology, Duke University, Durham, NC 27710, United States

Biological tissues are complex composite materials whose mechanical properties are often difficult to measure by traditional techniques. Quantification of bulk tissue properties, such as modulus and viscoelasticity, can be used in disease diagnosis and design of novel therapies. We demonstrate the ability to measure multiple types of mammalian tissues, with elastic moduli ranging from 100-10,000 Pa, by dynamic oscillatory rheology on a commercially-available rheometer. We begin by showing data collected from reduction mammoplasty human breast tissue isolated from multiple individuals and demonstrate that rheology can quantify tissue variability. Repeated freeze-thaw studies show the effect of sample history and highlight the need for consistent protocols for handling biological samples. We then move on to show results from two case studies involving tissue digestion by injected collagenase enzymes and illustrate how rheology can be used to quantify treatment efficacy. In the first, we used rheology to measure degradation of xenograft human breast cancer tumors grown in athymic nude mice. In the second, we used both rheology and histology to quantify the degree of in-vivo degradation of human uterine fibroid tissue. In both studies, we co-injected Liquogel (LQG), a thermoresponsive polymer that transitions upon heating from an injectable solution to a gel, to reduce diffusion of collagenase from the injection site. All tissues showed gel-like rheological behavior. We calculated average tissue moduli and extents of elasticity (tan  $\delta$ ) for all tissues. We observed that injections of LQG & collagenase significantly reduced tissue modulus compared to both buffer controls and free collagenase injections. Injection of LQG & collagenase also significantly increased the extent of elasticity. Finally, we demonstrate how atomic force microscopy measurements and histological staining of parallel tissue samples can be used alongside rheological measurements to gain a more complete understanding of treatment effects on tissues.

Monday 11:05 Tanglewood

BA4

### Constitutive modelling of human skin

Jibbe Soetens<sup>1</sup>, Gerrit Peters<sup>2</sup>, and Cees Oomens<sup>1</sup>

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Skin mechanics is important for research fields like pressure ulcer etiology and the interaction between skin and devices or materials such as shaving appliances. Prediction of the mechanical response of skin is essential. From a mechanical point of view, skin should be considered as a highly dynamic and complex composite that has non-linear viscoelastic, anisotropic and heterogeneous properties. The aim of this work was to develop a constitutive material model that is based on experimental evidence and capable of capturing the complex mechanical behaviour of skin. We implemented the constitutive model in a finite element code as a fibre-reinforced matrix with an elastic fibrous component and an isotropic, non-linear viscoelastic matrix. The fibres only contribute in extension and provide anisotropic properties. Heterogeneity was included by gradually varying the stiffness over skin thickness. Parameter optimization with respect to the experimental results was performed using an iterative parameter estimation method. Three intrinsically different experiments were performed on ex-vivo human skin. Large amplitude oscillatory shear (LAOS) combined with digital image correlation (DIC) on the cross-sectional area to assess heterogeneity resulting in the non-linear viscoelastic properties of the matrix. Secondly, biaxial tensile tests to determine the fibre contribution, again combined with DIC to determine local deformations and assess anisotropy. Finally, micro indentation experiments to determine the contribution of volume change. The model showed to be able to describe the non-linear viscoelastic response to LAOS. The anisotropic response of human skin to biaxial tensile loading was described more accurate than the well-established Ogden model. Overall our constitutive model is capable of describing the complex mechanical behaviour of human skin under shear, biaxial tension and indentation with a single parameter set.

## Symposium FP Food, Pharmaceuticals & Cosmetics

Organizers: Siva A. Vanapalli and Michael Boehm

Monday 9:50 Plaza II

FP1

### **Frictional and rheological behavior of multicomponent self-assembled gels**

Barbara V. Farias and Saad A. Khan

*Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

Aqueous gel systems containing polymers, oil, and phospholipids are widely used in personal care products. Phospholipids serve as an alternative to traditional surfactants to prevent skin irritation. In this study we use hydrogenated phosphatidylcholine (HPC) phospholipids, and two different crosslinked polyacrylic acid polymers, one of which is hydrophobically modified. Our goal is to examine the effect of composition on the rheological and tribological characteristics of the system and to establish relationships between these two properties to help predict sensory perception of skincare products. For tribology experiments we use a ball-on-disk configuration to obtain friction curves using different substrates to mimic the skin surface (PDMS and Bioskin(tm)). We use rheology to examine their behavior under small strain amplitude, as well as their behavior under nonlinear conditions using large amplitude oscillatory shear (LAOS). We examine how different concentrations of oil in the emulsion and polymers with different hydrophobicity affect friction and lubrication regimes from the tribological standpoint and the viscoelasticity, gel formation, and extent of nonlinearity from the rheological standpoint. The effect of each component is investigated by going from simpler to more complex systems. Systems containing a hydrophobically modified lightly crosslinked polyacrylic acid show lower yield stresses and lower moduli than systems with carbomer type polymer. We obtained Lissajous-Bowditch plots to get information about microstructural transition under large deformation. In the range of entrainment speed investigated in tribology experiments, the friction coefficients in the boundary regime are lower for systems containing the hydrophobically modified polymer than for systems containing the carbomer type polymer. The Stribeck curves obtained for each of the systems are compared for different polymer types and related to the rheology results to obtain physical insights into these complex systems.

Monday 10:15 Plaza II

FP2

### **Characterizing wear behaviors of casein gels by kernel-based modeling**

Juzhong Tan and Helen S. Joyner

*Food Science, University of Idaho, Moscow, ID 83844-2312, United States*

Hydrogels are soft materials that are used in bioprocessing, pharmaceutical, and food industries. Knowing their physicochemical properties, including durability, wear rate, and yield strength, is critical to understanding their functionality. The wear behaviors of hydrogels can be a good indicator for those properties. However, studies on hydrogel wear behaviors remains empirical and there is no wear model is available for characterizing wear properties. The objective of this study was to characterize the wear behavior of casein gels using a kernel-based statistical model. Casein gels (3-5% w/w concentration, 200mM NaCl) were evaluated under several normal forces (0.1-0.3 N). A kernel-based model was used to characterize gel wear behavior by breaking down the deformation-wear process into three successive regions: a deformation-dominant region, a constant wear rate region, and a failure region. A cubic function was used to model the deformation-dominant region and a linear function was used to fit the constant wear rate region. Wear rate and durability of gels were determined by the slope of constant wear rate region and the lengths of the first two regions respectively. Higher normal force and lower casein concentration resulted in higher constant wear rate, while the durability was shorter. The R<sup>2</sup> values of the cubic functions used to fit the deformation-dominant regions were >81.9%, indicating good fit. The cubic function parameters indicated that deformation at the beginning of the wear test was the main contributor to penetration depth. However, the deformation rate decreased and the wear rate increased with an increased number of contacts. In the constant wear rate region, wear was the main driver behind penetration depth increase. In the failure region, the gels underwent catastrophic surface failure, which caused a sharp increase in penetration depth. The model can be used to evaluate the functional properties of soft materials, as well as for targeted design of hydrogels with specific wear behaviors.

Monday 10:40 Plaza II

FP3

### **Effects of hydrocolloids, acids and nutritional supplements on gelatin network in gummies**

Haiyan Ge and Edward Shneyvas

*Product Research, Pharmavite LLC, Valencia, CA, United States*

Gelatin based gummy products provide elastic texture to consumers. The gelatin network in gummies and its gelation can be modified by hydrocolloids, acids and nutritional supplements. These effects have been investigated by dynamic rheological measurements. Hydrocolloids such as pectin, agar-agar can raise the gelation temperature of the gelatin network. Relative lower concentration of acids compared with gelatin can still maintain the elasticity of gelatin network with negligible gelatin denature. Nutritional supplements such as vitamin C, collagen and whey protein can interact with the random coils of gelatin to form strong gelling network and to delay the random coils transforming into partially ordered triple helices when gummy temperature decreases.

Monday 11:05 Plaza II

FP4

**Microrheological characterization of covalent adaptable hydrogels for applications in oral drug and nutrient delivery**Nan Wu and Kelly Schultz*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States*

Covalent adaptable hydrogels (CAHs) have dynamic covalent bonds, that reversibly degrade and reform in response to external stimuli, such as pH or shear. Due to this, CAHs have a wide range of applications including drug and nutrient delivery. Most previous characterization of CAHs has used bulk rheology, measuring the recovery of the material after a large applied strain. However, the inherent response to environmental conditions, like proposed applications, has been lacking. To bridge this gap, we use multiple particle tracking microrheology (MPT) to characterize pH induced CAH degradation, focusing on mimicking the gastrointestinal (GI) tract. The CAH we are characterizing is composed of 8-arm star poly(ethylene glycol)(PEG)-hydrazine and 8-arm star PEG-aldehyde. We characterize degradation of the CAH using MPT and  $\mu^2$ rheology, MPT in a microfluidic device. In MPT, fluorescent probes are embedded in the material and their Brownian motion is related to rheological properties. For  $\mu^2$ rheology, we use the device, that enables exchange of the incubation fluid with minimal sample loss to mimic temporal pH changes in the GI tract (between pH 4.3 and 7.4). First, we measure the degradation at a single pH (pH 4.3 or 7.4). At pH 4.3, the CAH degrades rapidly but also spontaneously re-gels without additional stimuli. At pH 7.4, the CAH degrades to the gel-sol transition and then oscillates around this transition until complete degradation. Next, we use our microfluidic device to characterize the CAH during consecutive degradation between pH 4.3 and 7.4. We determine that the change in material properties is consistent with control experiments. The time scale of pH 7.4 degradation is reduced when the scaffold is first degraded at pH 4.3 but there is no change when the material is first degraded at pH 7.4 subsequently at pH 4.3. Future  $\mu^2$ rheology experiments will mimic the complete GI tract to determine the viability of this material for sustained oral drug or nutrient delivery.

Monday 11:30 Plaza II

FP5

**The gluten is for stretch, but the bubbles define the elasticity of bread doughs**Sumana Chakrabarti-Bell*Food Science and Nutrition, University of Minnesota, St. Paul, MN 55108, United States*

When wheat flour is mixed with water and kneaded, proteins cross-link to form gluten and the mixture becomes a cohesive dough. The gluten structure imparts unique mechanical characteristics to doughs, underpinning the use of wheat in preparing a vast array of food products. The proteins in wheat are thought to provide the elasticity and strength to doughs, allowing bread to hold its shape. However, 3D micro-tomography studies, visualizing gas bubbles in doughs have shown that (1) bread dough is a foam made of numerous micro-scale gas bubbles, which partly coalesce during proofing and baking to form a single, open cell with a maze-like structure, (2) the sizes of gas bubbles affect the kinetics of dough rise and, (3) bubbles are larger in weakly elastic doughs. Investigations into fundamental rheological properties of doughs had shown that dough's elasticity is intrinsic to doughs, most likely driven by their mobility being trapped in doughs. A purpose-built, single roll-stand dough sheeter, instrumented with sensors for measuring roll forces and dough thickness, has been reported to be useful in testing flours for dough rheology. In order to better understand how flour types affect dough's elasticity, a study was undertaken to test a range of flours and doughs using the dough sheeter. In addition, the sheeted doughs were ultra-centrifuged to obtain dough's continuous, aqueous phase as the supernatant. Results showed that dough's strain-hardening and elasticity scaled with the ratio of volume and viscosity of the aqueous phase, not with protein amounts. It is known that the quality of the aqueous phase in doughs is affected by the non-starch polysaccharides present in flours. Simple bake tests performed with doughs containing additives that degrade polysaccharides showed that when the viscosity of the continuous phase was reduced, proofing rates decreased, bake volumes increased with crumbs containing smaller size bubbles. Results and plans for future work would be presented.



## Monday Afternoon

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Monday 1:30 Galleria I

SC6

#### **Comparing the response of colloidal glasses to transient stress- and strain-controlled shear**

Marco Laurati<sup>1</sup>, Tatjana Sentjabrskaja<sup>2</sup>, Jan Hendricks<sup>3</sup>, Alan R. Jacob<sup>4</sup>, George Petekidis<sup>4</sup>, and Stefan U. Egelhaaf<sup>2</sup>

<sup>1</sup>Universidad de Guanajuato, Leon, Mexico; <sup>2</sup>Heinrich-Heine University Düsseldorf, Düsseldorf, Germany; <sup>3</sup>KU Leuven, Leuven, Belgium; <sup>4</sup>IESL, FORTH, Crete, Greece

The rheological response of different colloidal glasses following either a step to a constant shear rate or to a constant stress (creep) is measured and the two responses are quantitatively compared [1]. To obtain different glasses (single, double and asymmetric glasses) we use a single model system, a binary mixture of colloidal hard spheres with different compositions and size ratios. Although the same steady state of flow is observed at long times, the transient responses in strain- and stress-controlled experiments differ significantly. To achieve yielding and a steady state of flow, less time and less energy input is required if a constant strain rate is applied. Moreover, larger strain rates or stresses result in faster yielding and flow, but require more total energy input. If a constant strain rate is applied, yielding and the transition to flow depend on the properties of the glass state, while much smaller differences are observed if a constant stress is applied.

[1] T. Sentjabrskaja, J. Hendricks, A.R. Jacob, G. Petekidis, S. U. Egelhaaf and M. Laurati, *J. Rheol.*, 62, 149 (2018)

Monday 1:55 Galleria I

SC7

#### **The transient behavior of soft glassy materials far from equilibrium**

Jun Dong Park and Simon A. Rogers

*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

The transient structural and rheological behavior of soft glassy materials out of equilibrium is studied under small, medium, and large amplitude oscillatory shearing and interpreted via the fully quantitative sequence of physical processes (SPP) technique. We identify features of the local strain distribution that cause particular rheological responses and show that the SPP metrics accurately reflect the structural transitions. The SPP modulus is shown to reflect how much of the imposed strain is stored in the form of recoverable elastic strain, establishing it as an accurate measure of structural elasticity. We demonstrate the ability of the SPP scheme to accurately determine the amount of recoverable strain acquired in elastically-dominated regimes by matching values estimated solely on the basis of the macroscopic stress to structural measures. In one case of large amplitude oscillatory shearing, the recoverable strain is shown to be around half a nondimensional strain unit by structural determination and from the SPP analysis, while the total imposed strain over the same interval is on the order of ten strain units. We therefore demonstrate the importance of separating the total and recoverable strains under strain-controlled conditions for the formation of accurate structure-property relations. We demonstrate how the alternating oscillatory state may be considered a consequence of a complex shear history. The results of this study show that the SPP scheme is a powerful tool for researchers wishing to understand the structural and rheological properties of soft glassy materials far from equilibrium.

Monday 2:20 Galleria I

SC8

#### **Meso-scale model of a soft glassy material under oscillatory shear**

Craig E. Maloney<sup>1</sup>, Kareem Khirallah<sup>1</sup>, Botond Tyukodi<sup>1</sup>, and Damien Vandembroucq<sup>2</sup>

<sup>1</sup>Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, United States; <sup>2</sup>PMMH, ESPCI, Paris, France

We study a meso-scale lattice model of a soft glassy material - a foam, emulsion, micro-gel paste, or dense granular packing - subjected to shear under cyclic loading. The model is based on the notion of local shear transformations which are the elementary objects from which continuum level constitutive laws (shear transformation zone theory, the soft glassy rheology model, etc.) are built. We subject the system to cyclic shear of various amplitude. We find that below a critical amplitude which we define as a yield strain, all rearrangements eventually cease after a (potentially very large) number of cycles, and the stress-strain curves become completely reversible with no hysteresis whatsoever. The characteristic number of cycles for cessation of rearrangement grows on approach to the yield strain consistent with a power-law divergence. Above the threshold, the system yields. The hysteresis loop narrows with time but eventually converges to a loop with finite area, and the tagged tracer particle statistics become diffusive. We discuss the complex patterns of shear localization which occur both in the transient (both above and below yield) and in the eventual steady state.

Monday 2:45 Galleria I

SC9

**Relationship between dynamical heterogeneity and rheology of soft particle glasses**Fardin Khabaz<sup>1</sup>, Michel Cloitre<sup>2</sup>, and Roger T. Bonnecaze<sup>1</sup><sup>1</sup>McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States; <sup>2</sup>ESPCI ParisTech, Paris, France

Soft particle glasses (SPGs) show a rich rheology under steady shear flow. At low shear rates, they show a solid-like behavior and yield stress, while at high shear rates they start flowing. The relationship between the shear stress and the applied shear rate is often expressed using the Herschel-Bulkley (HB) equation (e.g., Seth et al. Nat. Mater. 10, 838 (2011)) with an exponent of 0.5, but the origin of this exponent is not well-understood. Here, we employ a three-dimensional (3-D) particle-dynamics simulation to establish a link between the dynamics and rheology of the SPGs under steady shear flow. Interestingly, per particle stress calculations indicate that as long as there is a percolating cluster of particles with stresses smaller than the value of the yield stress, the suspension shows a solid-like behavior (i.e. yield stress), and the onset of the flow coincides with the breakage of this cluster of the particles. In addition, the average velocity of the particles shows a power-law behavior with an exponent  $\sim 0.75$  as a function of the shear rate that is consistent with the exponent seen in HB relationship of the flow curve. The analysis of particle dynamics reveals significant dynamic heterogeneities in suspensions under shear. The van Hove autocorrelation function, which is used to quantify the dynamic heterogeneities, shows a self-similar behavior at different times and shear rates. The van Hove function data can be collapsed onto a universal master curve after applying appropriate scaling factors, which are determined based on the long-time diffusion coefficient of particles. Results show that the relaxation time of the suspensions can be determined from the incoherent intermediate scattering function that can be utilized to predict the shear stress for these SPGs under steady shear flow. The origin of the exponent of 0.5 is discussed in relationship to the relaxation time for SPGs.

Monday 3:45 Galleria I

SC10

**Microstructure of sheared soft particles glasses near walls**Tianfei Liu<sup>1</sup>, Roger T. Bonnecaze<sup>1</sup>, and Michel Cloitre<sup>2</sup><sup>1</sup>University of Texas at Austin, Austin, TX, United States; <sup>2</sup>ESPCI ParisTech, Paris, France

Soft particle glasses (SPGs), concentrated suspensions of deformable particles, are viscoelastic materials that have a wide range of applications. One fundamental aspect of the rheology of SPGs is wall slip can occur during rheological characterization and their application. The wall slip is influenced by the roughness and surface chemistry of the wall. Furthermore, for weakly attractive surfaces, the shear rate can vary near the wall flow under simple shear flow, indicating that there must be local microstructural variations. The detailed microscopic origin behind these experimental observations is essentially unknown. To address this gap in understanding, a simulation tool is developed to predict the microstructure and rheology of SPGs being sheared between walls with varying roughnesses and interaction forces with the soft particles. In the simulation, all SPG particles are binned into layers according to their vertical positions with respect to the horizontal unidirectional flow between two parallel walls. The velocity of the particles is updated due to near-field pairwise interactions and far-field interactions so that the shear stress across all layers is constant. Results are presented for rough and smooth walls for neutral, repulsive and attractive interactions. As observed in experiments, the simulations show that SPGs do no slip over surfaces with roughnesses comparable to the size of the particles. On the other hand, the SPGs exhibit complete slip over walls with roughnesses much less than the size of the particles. The volume fractions are shown to be relatively constant across the gap in both these cases. Both attractive and repulsive wall-SPGs interaction forces are also investigated to understand their influence of slip over the wall with different surface chemistries. Analysis of the microstructure for these forces is presented for shearing with different wall roughnesses, including the velocity profile, concentration distribution and particle-distribution function across the gap.

Monday 4:10 Galleria I

SC11

**Oscillatory and history-dependent dynamics of shear banding in a thixotropic yield-stress fluid**Yufei Wei, Michael J. Solomon, and Ronald G. Larson*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States*

We use time-resolved particle image velocimetry with high spatial resolution to study the onset and evolution of shear bands in a fumed silica suspension, a thixotropic yield-stress fluid. This fluid exhibits rich spatiotemporal dynamics of local velocimetry, including shear bands that evolve slowly, quickly homogenize, and periodically oscillate, with no sign of these velocimetric dynamics in the bulk rheology. We construct a simple constitutive model to explain this phenomenology. This model contains two dynamical variables - one for thixotropy and the other one for kinematic hardening (KH). Different from previous thixotropic KH models, our model allows the KH effect to decay after flow stops, which is physically due to the rearrangement of internal structures. With this relaxation, the model successfully captures important features of experiments. It can be made more realistic by including additional dynamics that allows model parameters to undergo history- and time-dependent changes.

Monday 4:35 Galleria I

SC12

**Dynamics and reversibility of attractive colloidal dispersions: Influence of matrix viscoelasticity**Roberta Massaro<sup>1</sup>, Gabriele Colombo<sup>2</sup>, Christian Clasen<sup>1</sup>, Jan Vermant<sup>2</sup>, and Peter Van Puyvelde<sup>1</sup><sup>1</sup>Department of Chemical Engineering, KU Leuven, Leuven 3000, Belgium; <sup>2</sup>Department of Materials, ETH Zürich, Zürich, Switzerland

The balance of hydrodynamic and interparticle forces determines the microstructure of colloidal dispersions and their macroscopic behavior under flow. Flow can induce structural changes, which manifest in a variable viscosity that, if reversible and time dependent, is known as thixotropy.

The time scales associated with this structuration are typically longer than the classical viscoelastic time scales of the components but faster than phenomena such as ageing or degradation. In many relevant thixotropic systems, the suspending medium is viscoelastic. In that case there will be a competition between the time scale associated with the particulate network and the time scale associated with the inherent viscoelasticity of the matrix. The role of a viscoelastic medium was investigated here experimentally by studying PHSA stabilized PMMA particles dispersed in PDMS. Viscoelasticity was introduced by branching the polymeric chains. A rheo-confocal setup was implemented to monitor both microstructure and rheological behavior simultaneously. On one hand, using the counterrotating rheometer installed on the setup, stress contributions stemming from the different components in the dispersions could be analyzed as a function of the polymer matrix. On the other hand, by means of the high speed confocal microscope, equipped with structured illumination optics, we could study the structural evolution during steady state and transient flows. The strength of attraction between two primary particles was quantified to a) situate the system within the phase diagram with respect to the percolation limit and b) assess the reversibility. Moreover, particle tracking was used to study the influence of the matrix viscoelasticity on the particle dynamics, the evolution towards a steady-state and the reversibility of the system.

Monday 5:00 Galleria I

SC13

### **Diffusion and equilibrium structure of polydisperse colloidal suspensions confined by a spherical cavity**

Emma Gonzalez<sup>1</sup>, Christian Aponte-Rivera<sup>2</sup>, and Roseanna N. Zia<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Stanford University, Stanford, CA 94305-4125, United States;* <sup>2</sup>*Mechanical Engineering and Material Science, Duke University, Durham, NC 27705, United States*

Recent simulations of monodisperse colloidal suspensions confined by a spherical cavity demonstrate that both confinement and crowding produce qualitative changes in short and longtime transport rate processes and equilibrium material properties, arising from structural and dynamical heterogeneity associated with the confining cavity<sup>[1,2,3]</sup>. The theoretical and computational framework developed in these studies set the foundation for studying the dynamics of 3D microconfined suspensions. However, particle polydispersity in size, shape, and softness play a role in many biophysical confined systems such as the interior of eukaryotic cells<sup>[4]</sup>, but such effects in 3D confinement have received little attention in the literature. In the present work, we extend our spherically-confined Stokesian dynamics model to account for size polydispersity, which is known to exert pronounced effects on structure and rheology in unbound suspensions, including reduced viscosity, changes in phase behavior, and flow-induced size segregation. We present the hydrodynamic coupling functions and computational model for a polydisperse suspension of colloids coupled by many body hydrodynamic and lubrication interactions to one another and to the confining cavity. We utilize our model to study the combined effects of hydrodynamic interactions, Brownian motion, crowding and particle polydispersity on the equilibrium structure, as well as on the short- and long-time equilibrium transport properties of spherically confined polydisperse colloidal suspensions. These four effects exert a qualitative influence on particle diffusion and structure, which are discussed in detail.

[1] Aponte-Rivera and Zia, *Phys. Rev. Fluids*, 2016. [2] Aponte-Rivera, Su, and Zia, *J. Fluid Mech.*, 2018. [3] Aponte-Rivera, and Zia. Accurate 2-point microrheology inside a spherical cavity. In preparation. [4] Verkman, *Trends Biochem Sci*, Jan 2002.

## **Symposium FC Flow Assurance of Crude Oil & Derivatives**

Organizers: Monica F. Naccache and Rama Venkatesan

Monday 1:30 Plaza I

FC6

### **Kinetic and thermodynamic stability of surfactant stabilized water-in-diesel emulsion fuels**

Preetika Rastogi, Niket S. Kaisare, and Basavaraj G. Madivala

*Department of Chemical Engineering, Indian Institute of Technology - Madras, Chennai, Tamil Nadu 600036, India*

The total energy consumption of the world is expected to increase by almost 30% in the next two decades. There is therefore a need for environment friendly fuel alternatives and/or methods that reduce the consumption of conventional fossil fuels. While diesel engines are more efficient than gasoline engines, they have higher NO<sub>x</sub> and particulate emissions. Water-in-diesel emulsion fuels (EFs) are said to lower the peak combustion temperatures due to presence of micro- or nano water domains thereby reducing NO<sub>x</sub> emissions, whereas better atomization due to “micro-explosion” phenomenon is expected to reduce particulate emissions. A detailed analysis of surfactant-stabilized water-in-diesel EFs is presented, since these fuels could potentially be embraced with the existing engine technology and fuel supply infrastructure. As most EFs reported to date are kinetically stable, numerous reports that focus on the combustion characteristics of such fuels are available with little attention paid to their transportation and storage stability. In this work, first, the kinetically stable EFs, prepared by combination of two commercial surfactants, will be analyzed and their microstructure is visualized using optical microscopy to probe the effect of time and stabilizer concentration on the phase behavior and the stability. The change in their microstructure as a function of time provides an insight into their destabilization mechanism. To understand the morphology of thermodynamically stable EFs, droplet sizes of EFs formulated using a single surfactant have been investigated using dynamic light scattering technique and a comparison with kinetically stable formulations is presented thereof. We hence rationalize the phase behavior of microemulsions using this experimental data. We calculate the maximum amount of water that could be incorporated in thermodynamically stable formulation which greatly depends on the nature of oil used i.e., a n-alkane or diesel. Finally, the temperature stability of these EFs will also be presented.

Monday 1:55 Plaza I

FC7

**Role of interfacial rheology on the flow of pickering emulsions through a constriction**Indranil Sinha and Gordon F. Christopher*Texas Tech Univ, Lubbock, TX 79423, United States*

Over the past several years, we and several other groups have shown how interfacial viscoelasticity of particle laden interfaces can be controlled by altering surface, salt, or surfactant concentration. Although done in isolation, this work has been focused towards ultimately understanding how changes in interfacial behavior affect the bulk flow of Pickering emulsions, which has applications to commercial products, flow assurance, and petroleum processing. In this work, we directly examine how interfacial viscoelasticity is linked to bulk flow of Pickering emulsions using interfacial rheology, bulk rheology, and microfluidics.

The interfacial viscoelasticity of oil/water mixed silica nanoparticle/CTAB interfaces were characterized for a range of particle surface and surfactant concentrations; results were consistent with previous work in which increasing surface concentration or decreasing surfactant concentration created greater elasticity. Pickering emulsions with similar interfacial conditions were then produced and studied. The bulk rheology of these emulsions was examined and compared to interfacial results. Microfluidic constriction were used to examine droplet dynamics, drop size distribution and shape before and after the constriction, and pressure drop through the constriction. As interfacial viscoelasticity acts to stabilize the emulsion, we see less change in drop size distribution and decreasing coalescence of drops through the constriction. We believe these results will aid in understanding how to control the behavior of Pickering emulsions in a range of conditions.

Monday 2:20 Plaza I

FC8

**Pore blockage by emulsion injection in a microfluidic porous media**Gabriel Cruz, Jorge Avendaño, and Marcio S. Carvalho*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451900, Brazil*

Emulsion flooding is an enhanced oil recovery method that acts as a mobility control of the water phase. It acts by blocking pores where the waterflooding has left preferential paths, diverting water towards oil-filled pores. The effect of emulsion properties, such as drop size, and flow capillary number is probed by visualizing the flow through transparent glass micromodels that models a porous media. The micromodel is initially saturated with mineral oil, which is then displaced by water. Residual oil saturation is measured by imaging processing after the water and emulsion flooding steps. The results show that at the highest injection rate explored (higher capillary number), emulsion injection does not increase the volume of recovered oil. In contrast, at the lowest injection rate (lowest capillary number), oil ganglia that were immobile after water injection is displaced during emulsion injection. The volume of extra oil displaced is maximum when the oil drops of the emulsion is slightly larger than the pore throat diameter.

Monday 2:45 Plaza I

FC9

**The effect of demulsifiers in heavy oil production**Maria J. Moura, Botti C. Talita, Danmer Maza, Bruna C. Leopércio, Fernando S. Soares, Paulo R. Souza Mendes, and Marcio S. Carvalho*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451-900, Brazil*

Emulsion formation is a challenge when transporting heavy crude oil. Due to high viscosity, electric submersible pumps (ESPs) at the wellhead have been used to improve production. ESPs provide high shear rates to the flow, consequently increasing the formation of emulsions. The main challenge is that these emulsions have higher effective viscosity, increasing the pressure drop and hindering the flow. Emulsion destabilizers can be added at the entrance of an ESP in an effort to improve production. This work investigated the formation of emulsions of a Brazilian Sea heavy crude oil in a Stirred Tank under high shear rates. Several aspects of these emulsions were studied: the rheology, the continuous phase of the emulsion for different oil/water concentrations, the effective water concentration of the emulsions formed, the droplet size distribution, and the coalescence rate of the emulsions. Only water-in-oil emulsions are obtained. For a specific water content, however, a decrease in the effective viscosity of the solution is observed due to the appearance of free water during emulsion preparation. Two commercially available emulsion destabilizers - an emulsion breaker (EB) and an asphaltene inhibitor (AI) - were tested individually and in combination. No change was observed with the addition of the AI alone. However, in combination with the EB the amount of water released from the emulsion was significantly larger than in the presence of the EB alone. The addition of different concentrations of emulsion destabilizers changed the range of water concentration at which free water occurs. The emulsions with demulsifiers presented instability after days at rest, different from the emulsions without these additives. This study provides fundamental understanding of crude oil emulsion formation in rotating and high shear systems and in the presence of emulsion destabilizers.

Monday 3:45 Plaza I

FC10

**Dense suspensions of hollow glass beads in a shear thinning fluid**John P. Singh<sup>1</sup> and Ron G. Morgan<sup>2</sup><sup>1</sup>Halliburton, Houston, TX 77032, United States; <sup>2</sup>Halliburton, Duncan, OK 73536, United States

Hollow glass spheres (beads) are widely used as density and rheological modifiers for various oil and gas process fluids, particularly cement. One of the primary uses is to achieve lightweight slurries with good mechanical properties of the set cement. This paper discusses a concentrated yet pumpable suspension of these spheres for offshore cementing applications. Providing the lightweight spheres in a liquid suspension eliminates the risks associated with dry blending these materials. Development of the liquid suspension of hollow beads enables on-the-fly mixing of cement

slurries with desired density profiles. This work presents the rheological behavior of the concentrated suspension (up to 60% v/v) of hollow glass spheres suspended in a dilute aqueous solution of viscosifier and pH control agent. A rheological model was developed to highlight the bead-bead surface interactions as a major component controlling flow behavior. Four different variants of beads were studied. These were selected to represent a range in surface area per unit volume of beads. Increasing the concentration of beads or the viscosifier in solution correlated to increased yield stress and apparent viscosity at operational shear rates. In addition, a Krieger-Dougherty-type relation adequately quantifies the effect of bead concentration, with the maximum packing fraction of beads being a function of surface area per unit volume of the beads. Overall, the Herschel-Bulkley (HB) model best describes the suspension rheology with the shear thinning exponent in the range of  $-0.8$  to  $1$ . Surface area of the beads linearly correlates to the yield stress of the corresponding concentrated bead solution.

Monday 4:10 Plaza I

FC11

### **Microstructure and rheological characteristics of asphalt binders**

Liyan Shan<sup>1</sup>, Norman J. Wagner<sup>2</sup>, Zhuang Li<sup>1</sup>, Hongsen He<sup>1</sup>, and Ru Xie<sup>2</sup>

<sup>1</sup>*School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin, China;* <sup>2</sup>*University of Delaware, Newark, DE, United States*

Asphalt binder is an important component used in pavement. The microstructure and rheological characteristics of it are critical to pavement performance, hence they are the focus of much research in the past few decades. However, the microstructure of asphalt binders and how this is coupled to its rheological behavior is still not clear. Furthermore, most of the rheology research focuses on the linear rheological behavior rather than the nonlinear rheological behavior that may be associated with performance and failure of asphalt. The literature shows that SANS is an effective tool to reveal the nanoscale microstructure, and LAOS is useful to study the nonlinear rheological behavior of colloidal materials. To address the need for improvements in structure-property relationships in the field of asphalt research, the microstructure and nonlinear rheological behavior of asphalt binders were studied using SANS and LAOS. We studied five different kinds of asphalt binders and one type of SBS modifier using SANS. The results reveal the microstructure of asphalt binders and SBS polymer changing with temperatures. It also provides further evidence for colloid structure of asphalt binder and mechanism of SBS modification. The LAOS stress rheological response of both a neat bitumen and a modified bitumen are analyzed by FT-rheology and strain decomposition to an orthogonal set of Chebyshev polynomials. We find that the relative nonlinearity of bitumen increases with increase in stress and decrease in frequency; the intrinsic nonlinearity  $Q_0$  decreases with increase in frequency and decrease in temperature. Bitumen A exhibits stress softening and stress thinning under all the studied test conditions, but bitumen B exhibits stress stiffening under some conditions. The structure-property relationships for asphalt binders were studied by comparing the SANS and LAOS results. The results show that the microstructure of asphalt binder affects the rheological behavior of asphalt binder, especially the modifier in the asphalt.

Monday 4:35 Plaza I

FC12

### **Displacing viscous heavy oil via emulsification with alkali-surfactant foam in micromodels**

Eric D. Vavra, Maura Puerto, George J. Hirasaki, and Sibani Lisa Biswal

*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Recently, alkali-foam enhanced oil recovery (EOR) has been studied as a promising method for mobilizing heavy oil via its emulsification in the aqueous phase that simultaneously improves volumetric sweep efficiency. In this presentation, a procedure is described for optimizing a novel alkali-foam EOR process the recovery of heavy oil. Key steps in the procedure help to ensure successful oil recovery; for example, phase behavior analyses at the injection condition and the reservoir condition provide novel insight into the fluid properties one might expect in an EOR scenario. Visual studies were performed in a micromodel to examine the relevant fluid dynamics in a porous media environment and to gain an understanding into the emulsion-viscosity interplay of the system.

Monday 5:00 Plaza I

FC13

### **Optical and rheological analysis of waxy crude oils microstructure: Applications to flow assurance control**

Consiglia Carillo<sup>1</sup>, Salvatore Coppola<sup>2</sup>, and Sergio Caserta<sup>1</sup>

<sup>1</sup>*DICMAPI, University of Naples Federico II, Naples, Italy;* <sup>2</sup>*Research Department, Versalis S.p.A., Naples, Italy*

Upstream of non-conventional oils is one of the key challenges in energy supply. The presence of high molecular weight fraction can induce high relevant temperature variation in the oil rheology, due to formation of crystals and nucleation of gelly phases, leading to a common problem known as "Flow Assurance". The high variability of oil composition makes prediction and control of its rheology a difficult task, that can lead to catastrophic blocking of pipes. The scope of this work is to analyse the crystallization phenomena of waxy crude oils. In particular we propose here a novel technique based on microscopy observation and image analysis to characterize Wax Appearance Temperature (WAT) and crystallization kinetic. Our technique is compared the typical methods of rheology and calorimetry, usually used to characterize and control crude oil properties. The comparison of different techniques can provide wider understanding of fluid microstructure. Furthermore, the methodology we propose is able to estimate the initial formation of crystals several degrees above the rheology measured WAT. Our technique can be used as a predictive tool, able to foresee the increment in oil moduli when the fluid rheology is still unaffected by the change in morphology.

## Symposium AM Additive Manufacturing

Organizers: Anthony Kotula and Patrick Anderson

Monday 1:30 Bellaire

AM6

### **From liquid ink to solid object: Tailoring the microstructure of additively manufactured freeform macrostructures through extensional rheology-mediated extrusion**

Crystal E. Owens, A. John Hart, and Gareth H. McKinley

*Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Additive manufacturing through direct-ink writing constructs 3D objects via the buildup of a filament, and the capabilities of the final part rely directly on the properties of the ink. Commonly, rigid rod-like particles such as carbon nanotubes or glass fibers are added to starting materials in low concentrations as reinforcement or “filler” for end-use 3D-printed parts, substantially improving strength and toughness. In addition, direct printing of electrically conductive materials can enable entirely new functional geometries, such as field emitting devices.

Meanwhile, fiber-spinning processes can create processed structures with the highest specific strength relative to other traditional manufacturing methods (such as molding or extrusion), when using the same starting material. This is because of the additional external control over the development of microstructure during the processing operation, particularly from flow-induced crystallization of polymer chains and/or orientation of rigid rod-like structures from the strong extensional kinematics. Using these extensional flows along with 3D printing can enable microstructure control.

In this work, we study the flow-mediated structure evolution of rigid rod-like particle-based inks, especially using single-walled carbon nanotubes (SWCNTs) dispersed in water, dimethylformamide, or ionic liquids at concentrations from 0.1-1%wt, inside a bespoke microfluidic spinneret nozzle designed to impose extensional flow and control the tension at all locations along the forming filament. We report the influence of processing parameters such as the ratio of the sheath and filament flow rates, rate of elongation, and rate of solvent exchange, on the strength, conductivity, and dimension of the extruded filament and of the final printed object, and develop scaling relationships that connect these to the rheological properties of the ink.

Monday 1:55 Bellaire

AM7

### **Simulation of rheological effects in processing during material extrusion**

Jeffrey S. Horner<sup>1</sup>, David D. Phan<sup>1</sup>, Keith Coasey<sup>2</sup>, Antony N. Beris<sup>1</sup>, and Michael E. Mackay<sup>2</sup>

<sup>1</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States;* <sup>2</sup>*Materials Science and Engineering, University of Delaware, Newark, DE, United States*

Material Extrusion (ME, sometimes called Fused Filament Fabrication (FFF) or Fused Deposition Modeling® (FDM)) is an additive manufacturing technology where a solid fiber of polymer (ca. 1-3 mm in diameter) is driven into a cylindrical, heated sleeve whereupon it melts. The molten polymer seals around the solid fiber, so, it acts as a piston driving itself through a conical nozzle. The pressurized melt is pushed through the orifice to make a filament (ca. 0.5 mm in diameter) that is deposited onto a moving substrate to make an object. We simulate the melting and flow processes using a finite volume technique to find both are complicated. Complex flow patterns develop within the heated sleeve until the fiber is completely melted then non-Newtonian effects come to bear as the melt enters the converging nozzle. A technique was developed to measure the pressure in the nozzle and it is compared to the predicted pressure to find they are adequately correlated. Future research will center on optimizing the heated sleeve and nozzle to allow faster processing and to incorporate viscoelastic effects using the finite element simulation technique that are particularly important in the nozzle.

Monday 2:20 Bellaire

AM8

### **Nonisothermal welding in fused filament fabrication**

Keith Coasey<sup>1</sup>, Kevin R. Hart<sup>2</sup>, Eric Wetzel<sup>2</sup>, David Edwards<sup>3</sup>, and Michael E. Mackay<sup>4</sup>

<sup>1</sup>*Materials Science and Engineering, University of Delaware, Newark, DE, United States;* <sup>2</sup>*Materials and Manufacturing Sciences Division, U.S. Army Research Laboratory, Aberdeen, MD, United States;* <sup>3</sup>*Department of Mathematical Sciences, University of Delaware, Newark, DE, United States;* <sup>4</sup>*Materials Science & Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Fused filament fabrication (FFF), sometimes called material extrusion (ME) offers an alternative option to traditional polymer manufacturing techniques to allow the fabrication of objects without the need of a mold or template. However, these parts are limited in the degree to which the welding interface is eliminated post deposition, resulting in a decrease in the interlaminar fracture toughness relative to the bulk material. Here we have utilized reptation theory under nonisothermal conditions to predict the development of healing over time, from the rheological and thermal properties of Acrylonitrile-Butadiene-Styrene (ABS). ABS is rheologically complex and acts as a colloidal suspension and as such considerations had to be made for the time of relaxation of the matrix which is important in predicting the degree of interfacial healing. The nonisothermal healing model developed is then successfully compared to experimental interlaminar fracture experiments at variable printing temperatures, allowing future optimization of the process to make stronger parts.

Monday 2:45 Bellaire

AM9

**Welding of 3D printed carbon nanotube-polymer composites by locally induced RF heating**Micah J. Green<sup>1</sup>, Charles B. Sweeney<sup>2</sup>, and Mohammad A. Saed<sup>3</sup><sup>1</sup>Chemical Engineering, Texas A&M University, College Station, TX 77843, United States; <sup>2</sup>Texas A&M University, College Station, TX 77843, United States; <sup>3</sup>Texas Tech University, Lubbock, TX 79409, United States

Additive manufacturing through material extrusion (ME), often termed 3D printing, is a burgeoning method for manufacturing thermoplastic components. However, a key obstacle facing 3D-printed plastic parts in engineering applications is the weak weld between successive filament traces, which often leads to delamination and mechanical failure. This is the chief obstacle to the use of thermoplastic additive manufacturing. Here we report a novel concept for welding 3D-printed thermoplastic interfaces using intense localized heating of carbon nanotubes (CNTs) by radio frequency (RF) irradiation at microwave frequencies. The microwave heating of the CNT-polymer composites are a function of CNT percolation, as shown through in situ infrared imaging and simulation. We apply CNT-loaded coatings to 3D printer filament; the ability to coat and print these structures involve both solution- and melt-rheological tuning as a function of CNT loading. After printing, RF irradiation is shown to improve the weld fracture strength by 275%. These remarkable results open up entirely new design spaces for additive manufacturing and also yield new insight into the coupling between dielectric properties and RF field response for nanomaterial networks.

Monday 3:45 Bellaire

AM10

**Selective laser sintering of polymer particle pairs studied by in-situ visualization**Prakhyat Hejmady, Ruth Cardinaels, Lambèrt van Breemen, and Patrick D. Anderson*Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant, The Netherlands*

Selective laser sintering (SLS) is a 3D printing technology. During this manufacturing process polymers undergo a varying temperature profile during which the particles partially melt and thereby sinter together resulting in a complex microstructure. Incomplete sintering of the polymer particles, results in significant remaining porosity as well as limited interlayer adhesion resulting in poor mechanical properties of products. Therefore a dedicated experimental setup, which incorporates the main features of a SLS machine and at the same time allows in-situ visualization of the sintering dynamics by means of optical microscopy and X-rays, is developed. A visible-light laser is used to achieve good spatial resolution and control over the supplied energy. Initial thermal characterization by DSC enabled us to define the stable sintering region for the particles as well as their thermal properties. The energy absorption of the polymers containing a black dye was measured as a function of layer thickness and dye content. In addition, the polymers were rheologically characterized at various temperatures to assess rheology effects in the sintering process. Subsequently, sintering experiments were conducted on amorphous polymers, wherein pairs of polymer particles were subjected to a known amount of laser energy inside a temperature controlled chamber. By tracking the dynamics of the neck growth between the particles, the sintering behavior was correlated to the material and processing conditions. The potential of existing theoretical [1] and numerical models [2] for viscous sintering under isothermal conditions was explored. The combination of a full material characterization with sintering experiments under well-defined conditions will pave way for rational material design in SLS, a process that up to now was mainly based on trial-and-error.

[1] Pokluda, O, et al. AICHE journal, 43(12), 3253-3256, (1997) [2] Baemans, C, et al. Applied Sciences, 7,5:516, (2017)

Monday 4:10 Bellaire

AM11

**A comparison of the cold spray deposition process to micro-ballistic single particle impact experiments for polymer powders**Zahra Khalkhali, Wanting Xie, Jae-Hwang Lee, and Jonathan Rothstein*Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, MA, United States*

Cold spray is a solid-state additive manufacturing technique which utilizes supersonic gas flow to accelerate particles through converging-diverging nozzles to create a smooth, low-porosity coating upon impact on a substrate. In this work, a cold spray system capable of accelerating 10 - 100micron polymer particles up to Mach 2 to deposit a variety of polymers including HDPE, PUR, PS, PA, UHMWPE and PEEK on a host of different substrates was employed. Windows of successful deposition will be presented over the velocity - temperature space for various particle/substrate choices and the effect of the polymer properties including glass transition temperature on the shape of the deposition window will be discussed. A series of laser-induced micro-ballistic single particle impact experiments will be presented with impact velocities and temperatures similar to the cold spray experiments so that the results can be directly compared to further understand the impact behavior and bonding mechanisms powders during deposition. We will demonstrate the importance of the role of successive particle collisions in cold spray as the resulting peening effect was found to dramatically improve the deposition efficiency and adhesion strength of the coating. This peening effect will be investigated further as a means towards improving deposition efficiency by adding non-adhering micron-size glass beads to the polymeric particle batches in the cold spray technique. The dynamics of the cold spray and micro-ballistic particle impacts will be presented through high-speed imaging detailing the flight, impact and rebounding of the particles. Results from SEM studies will be presented to analyze plastic deformation as a function of impact velocity, temperature and polymer. Trend in the critical strain for bonding and energy dissipation percentage at various impact velocities will also be presented to help design processes conditions that maximize deposition efficiency and the final coating quality.

Monday 4:35 Bellaire

AM12

**Computational modeling of the selective laser sintering process**Caroline Balemans, Martien A. Hulsen, and Patrick D. Anderson*Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands*

Selective laser sintering is an upcoming 3D printing technique for industrial applications. It is one of the techniques using polymer powder as building material. The polymer powder is locally heated in a layer-by-layer manner. The powder that is not sintered acts as support material during the fabrication process, enabling a large freedom of geometry. To ensure the quality of the printed objects, we need to understand the relation between the process and the mechanical properties of the products. We developed a computational model using the finite element method to assess the sintering process in detail. First, we analyzed the flow problem of the sintering mechanism of two viscoelastic particles. Both the Giesekus model and the eXtended Pom-Pom model [1] are used to describe the complex behavior of the polymer. From the study of the conformation tensor, which is a measure for the polymeric strain, we concluded that crystallization may play an important role in the final microstructure of the printed products [2]. Next, we included the temperature-dependent flow behavior of the particles. By varying the process and material parameters, we studied the effect on the sintering of the particles. In this talk we will present the results of both the viscoelastic flow and the temperature-dependent behavior of the system. The final step is to include the crystallization kinetics, such that we can predict and tune the morphology of the final products using the process parameters. We hope to present some first results of the crystallization study at the meeting as well.

References: [1] W.M.H. Verbeeten, G.W.M. Peters, F.P.T. Baaijens, Differential constitutive equations for polymer melts: the eXtended Pom-Pom model, *Journal of Rheology*, 2001, 45, 823-843. [2] C. Balemans, M.A. Hulsen, P.D. Anderson, Sintering of two viscoelastic particles: a computational approach, *Applied Sciences*, 2017, 7, 516.

Monday 5:00 Bellaire

AM13

**Quantification of isothermal crystallization of polyamide 12: Modelling of crystallization kinetics and phase composition**Fabio Paolucci and Gerrit Peters*Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands*

The crystallization of Polyamide 12 (PA12) has been investigated using a new experimental setup which allows in-situ synchrotron Wide Angle X-ray Diffraction (WAXD) during Flash-DSC measurements. The experimental results are used to parameterize and validate a new numerical model to quantify the quiescent crystallization kinetics of the three important crystal structures of PA12, i.e. the  $\gamma$ -,  $\alpha'$ - and mesomorphic phase. The experimental approach is based on nucleation and growth after quenching the material from the melt to an isothermal temperature, described by the Schneider rate equations and the Kolmogorov-Avrami expression for the space filling. The experimental overall crystallization rate, expressed in terms of the crystallization half-time, as well as the phase composition, are well captured by the model over a wide range of temperatures, i.e. between the glass transition and the melting temperature. It is shown that at temperature below and above 100 °C different nucleation mechanisms are dominant causing the bimodal dependence of the crystallization rate.

## Symposium PS Polymers in Solution

Organizers: Nicolas J. Alvarez and Cari Dutcher

Monday 1:30 Post Oak

PS6

**Assessment of the evaporation-induced strength development of polymer solutions used for membrane applications: A shear rheometry protocol**Eduard A. Caicedo-Casso<sup>1</sup> and Kendra Erk<sup>2</sup>*<sup>1</sup>MSE, Purdue University, West Lafayette, IN 47907, United States; <sup>2</sup>Materials Engineering, Purdue University, West Lafayette, IN 47906, United States*

Shear rheometry was used to directly quantify the flow behavior of polymer solutions under minimal and significant solvent evaporation conditions. The studied polymer solutions are the most common polymer systems used to fabricate isoporous asymmetric membranes by the self-assembly and non-solvent induced phase separation (SNIPS) method. Three different A-B-C triblock terpolymer chemistries of similar molar mass were evaluated: polyisoprene-b-polystyrene-b-poly(4-vinylpyridine) (ISV); polyisoprene-b-polystyrene-b-poly(N,N-dimethylacrylamide) (ISD); and polyisoprene-b-polystyrene-b-poly(tert-butyl methacrylate) (ISB). The viscosity of each polymer solution under minimal evaporation was found to be a function of the physicochemical properties of individual polymer chains. Conversely, significant solvent evaporation resulted in the formation of a viscoelastic film typical of asymmetric membranes. The film viscoelasticity was strongly dependent on the chemical structure of the triblock terpolymer molecules as well as their ability of forming a long-range organization (as demonstrated by collaborators). A hierarchical magnitude (ISV>ISB>ISD) was observed for viscosity and strength development, with ISV solutions displaying the greatest solution viscosity, fastest film strength development, and greatest strength magnitude. The demonstrated relationship between the chemical structure of block copolymers and the viscoelastic response of SNIPS membranes is another link to get researches closer to the upscaling of the SNIPS process.



Monday 1:55 Post Oak

PS7

**Tailoring pore morphology in the polymer films fabricated via dry cast phase separation technique**Rumiya Pervin and Basavaraja Gudappa*Chemical Engineering Department, Indian Institute of Technology, Chennai, Tamilnadu 600036, India*

Porous polymer films with controlled pores have drawn significant attention in recent years in the field of aerospace, automotive, control drug delivery, membrane, selective adsorbents etc. Porous polymer also find potential application as catalyst supports, antireflection coatings, light weight structural materials, template for inorganic growth masks etc.[1] As a main objective of this work, we represent a simple Dry-Cast Phase Separation (DCPS) technique [2] for fabricating ordered porous structure in polymeric film and explain mechanism involved in the process. This process was used for PMMA (polymethyl methacrylate) microporous film synthesis by casting a homogeneous solution of PMMA-THF-water. The influence of water, polymer content and the casting volume on the film morphology was studied. In several cases, evaporation of THF leads to the formation of water droplets due to phase separation. Upon evaporation of water, a porous film was formed. We investigated the phase separation mechanism by constructing PMMA-THF-water phase diagram experimentally. During film formation, the composition as well as viscosity of the medium would vary with time due to evaporation of both THF and water. We show that depending on the composition path during drying, the morphology of film varied from porous to nonporous or a composite film with surface pores alone. A mechanistic understanding of the film formation and dependence of the composition path on film morphology will be discussed.

References: [1] Y. Wang, Z. Liu, B. Han, Z. Sun, J. Zhang, D. Sun, Phase-Separation-Induced Micropatterned Polymer Surfaces and Their Applications, *Advanced Functional Materials*, 15 (2005) 655-663. [2] M. Ulbricht, *Advanced functional polymer membranes*, *Polymer*, 47 (2006) 2217-2262.

Monday 2:20 Post Oak

PS8

**Temperature and concentration behavior of the viscosity of lubricating oil-polymer viscosity index improvers: Thermodynamic (TV<sup>γ</sup>) scaling versus T-T<sub>g</sub> scaling**Sixue Cheng and Gregory B. McKenna*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Polymeric additives are commonly used as viscosity index improvers (VII) for lubricating oils in order to improve viscosity-temperature performance. The mechanism behind VII is still in debate. Here, we study the VII's effect from a new perspective: the viscosity-temperature relationship (viscosity improvement) is modified by the polymeric VII because of a change in both the T<sub>g</sub> and the dynamic fragility m. We further consider the behavior in terms of TV<sup>γ</sup> scaling and T-T<sub>g</sub> scaling or shifting. Eleven pairs of polymer/oil mixture data from the published literature have been reanalyzed to obtain the relationship between polymer concentration versus viscosity index, T<sub>g</sub> and m. The results show that poly(alkyl methacrylate) type VII systems behave differently from hydrocarbon VII systems. In addition, comparison of thermodynamic scaling TV<sup>γ</sup> and T-T<sub>g</sub> shifting for twelve polymer solutions over a wide concentration and temperature range show that, a modified T-T<sub>g</sub> shifting works for most cases, while thermodynamic scaling breaks down for many polymer solution systems. Implications of the results are discussed.

Monday 2:45 Post Oak

PS9

**Entangled polymer chains relax via dynamically heterogeneous pathways**Yuecheng Zhou<sup>1</sup> and Charles M. Schroeder<sup>2</sup>*<sup>1</sup>Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; <sup>2</sup>Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Stress relaxation following deformation of an entangled polymeric liquid is thought to be affected by transient reforming of chain entanglements. In this work, we use single molecule techniques to study the relaxation of individual polymers in the transition regime from semi-dilute unentangled to entangled solutions. In particular, we directly observe the relaxation dynamics of linear tracer polymers in background solutions of linear entangled polymers across a wide range of concentrations spanning  $c_e < c < c^*$ . Our results reveal the emergence of dynamic heterogeneity underlying polymer relaxation behavior, including distinct molecular sub-populations described by a single-mode and a double-mode exponential relaxation process. Interestingly, this dynamic behavior starkly contrasts polymer relaxation in dilute and semi-dilute unentangled solutions. As polymer concentration is increased from  $\sim 3 c^*$  to  $\sim 15 c^*$  (spanning  $\sim 1 c_e$  to  $\sim 5 c_e$ ), the fraction of molecules that exhibit single-mode exponential decay behavior decreases, whereas the fraction of double-mode exponential trajectories increases, with nearly all relaxation trajectories showing a double exponential response at high concentrations. In all cases, we interpret the power law scaling of these characteristic relaxation times as a function of concentration. The slower double-mode timescale is consistent with a characteristic reptation time, whereas the single-mode timescale and the fast double-mode timescale are attributed to local regions of transient disentanglement due to deformation. These results are discussed and rationalized in the context of existing molecular and phenomenological models of entangled polymer solutions such as the classic tube model and recent extensions. Taken together, these results reveal fundamentally new information regarding the behavior of polymer chain relaxation for lightly entangled solutions.

Monday 3:45 Post Oak

PS10

**Nonhomogeneous flows during startup shear of highly entangled polystyrene solutions**Michael C. Burroughs, Matthew E. Helgeson, and L. Gary Leal*Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

Constitutive models for entangled polymer solutions have received continual refinement to incorporate the mechanisms of reptation, chain stretch, convective and reptation-based constraint release, and contour length fluctuations. The success of these models is commonly assessed by the ability to fit rheological data. However, increasing experimental evidence suggests that the effect of constitutive behavior on flow is an important consideration for further model development. Here, we present new experimental evidence from simultaneous rheological and particle tracking velocimetry (rheo-PTV) measurements in Taylor-Couette flow of anomalous flow in startup of steady shear of entangled solutions of polystyrene in dioctyl phthalate with otherwise expected rheological behavior. Specifically, we find reasonable agreement in measured rheology under steady shear compared to Rolie-Poly constitutive model predictions for solutions with varying entanglement number,  $Z$ . For low  $Z$ , predictions of the Rolie-Poly model are also in agreement with transient shear stress and flow velocimetry data. However, for  $Z > 30$ , strong departure from the Rolie-Poly predictions of the flow kinematics are observed. Interestingly, we find steady state velocity profiles that resemble shear banding, with gradients in shear rate that oppose the inherent stress gradient of Taylor-Couette flow. PTV measurements of the transient response of these solutions' flow kinematics under startup of steady shear provides a potential explanation for this previously unobserved and unpredicted behavior. Overall, the results indicate that monotonic constitutive behavior does not preclude the possibility of nonhomogeneous flow of polymer solutions, and highlights the importance of simultaneous flow visualization and rheological measurement to test rheological models for entangled polymer solutions under nonlinear flows.

Monday 4:10 Post Oak

PS11

**Conformational averaging as a route to incorporating hydrodynamic interactions into simulations of dilute and semidilute polymers**Charles E. Sing<sup>1</sup> and Charles D. Young<sup>2</sup>*<sup>1</sup>Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States; <sup>2</sup>University of Illinois at Urbana-Champaign, Urbana, IL, United States*

Solution-processing methods typically involve polymer concentrations in the semidilute range, where polymer coils impinge on each other and 'overlap'. This is particularly true when polymers are driven out-of-equilibrium by strong processing flows, and polymer dimensions are extended in the flow direction. Despite the practical importance of such systems, they are difficult to simulate due to the computational expense required to include hydrodynamic interactions (HI); yet, HI is necessary to capture the correct polymer dynamics. We have developed a new "Conformational Averaging" (CA) method for incorporating HI into semidilute polymer dynamics, in a way inspired by classical theoretical efforts in single-molecule kinetic theory. CA is an iterative procedure that uses an averaged hydrodynamic tensor in Brownian Dynamics simulation, which is used to get a new hydrodynamic tensor averaged over the simulation trajectory. We are able to simulate both dilute and semidilute solutions rapidly, and explore molecular diffusion and relaxation, as well as hydrodynamic screening. We show standard scaling laws in equilibrium, including how HI screening length behaves as polymer concentration increases.

Monday 4:35 Post Oak

PS12

**Brownian dynamics simulations of semidilute polymer solutions in extensional flow**Charles D. Young and Charles E. Sing*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States*

The dynamics of semidilute polymer solutions are governed by a relationship between solvent-mediated hydrodynamic interactions (HI), solvent quality, topological constraints, and flow. Unlike dilute and concentrated solutions, which can often be understood using mean-field theories and scaling concepts, semidilute solutions exhibit large fluctuations in the local concentration which generally preclude approximate models. This challenge is particularly relevant when the solution is driven out of equilibrium by a strong flow. Perturbations to the external flow caused by intramolecular and intermolecular HI become coupled to the polymer conformation, meaning molecular predictions of the macroscopic solutions properties are not straight forward. We perform Brownian Dynamics (BD) simulations to reveal the connection between HI and flow strength for semidilute polymer solutions in extensional flow. Using our recently developed Iterative Conformational Averaging method to accelerate to computation of the HI and correlated Brownian noise, we first verify our simulations by comparison of the polymer stretch and extensional viscosity to experimentally measured values. Then we investigate the effects of flow rate on the hydrodynamic screening length as an extension of the equilibrium case where only concentration effects are considered. We discuss the significance of the flow effects and suggest applications for these simulation results.

## Symposium ET Advanced Experimental Techniques/Methods in Rheology

Organizers: Kalman Migler and Simon Rogers

Monday 1:30 San Felipe Room

ET6

### Using extensional viscosity to determine the length (or molecular weight) of rod-like molecules, and its importance in studying the phase behavior of carbon nanotube solutions

Matteo Pasquali<sup>1</sup>, Dmitri E. Tsentalovich<sup>1</sup>, Anson Ma<sup>2</sup>, Jun A. Lee<sup>1</sup>, Natnael Behabtu<sup>1</sup>, Elie A. Bengio<sup>1</sup>, Robert J. Headrick<sup>1</sup>, Micah J. Green<sup>3</sup>, and Ishi Talmon<sup>4</sup>

<sup>1</sup>Department of Chemical & Biomolecular Engineering, Rice University, Houston, TX 77005, United States; <sup>2</sup>Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06268, United States; <sup>3</sup>Chemical Engineering, Texas A&M University, College Station, TX 77843, United States; <sup>4</sup>Chemical Engineering, Technion Israel Institute of Technology, Haifa, Israel

Intrinsic viscosity is the oldest, simplest method for determining the molecular weight of a polymer. For polymer coils, the method is based on measuring the shear viscosity of a dilute polymer solution at low enough shear rate that the polymer conformation is unaffected by the viscous forces. The method fails for progressively longer, rod-like molecules, as the longest relaxation time scales with the cube of molecular weight (length) in rods (vs. the 1.5 to 1.8 power for coils in theta or good solvents). We develop a new method for measuring the length of rod-like molecules in extensional flows. The method is based on measuring the extensional viscosity of solutions of rod-like polymers with a customized capillary thinning rheometer. It relies on the relative ease of aligning rods in extensional flow, combined with the theoretical relation between extensional viscosity and aspect ratio in semidilute solutions of aligned rods. We demonstrate that this method can determine the aspect ratio of carbon nanotubes (CNTs) simply and accurately. We measure CNT diameter  $d$  by transmission electron microscopy (TEM) and arrive at CNT length  $L$ . By studying CNT samples synthesized by different methods, we show that the method works well for CNT lengths ranging from 0.4 to at least 20  $\mu\text{m}$ , a wider range than for previous techniques. Moreover, we measure the isotropic-to-nematic transition concentration (i.e., isotropic cloud point)  $f^*$  of CNT solutions and show that this transition follows Onsager-like scaling  $f^* \sim d/L$ . We characterize the length distributions of CNT samples by combining the measurements of extensional viscosity and transition concentration and show that the resulting length distributions closely match distributions obtained by cryo-TEM measurements. Interestingly, CNTs appear to have relatively low polydispersity compared to polymers and high polydispersity compared to colloidal particles.

Monday 1:55 San Felipe Room

ET7

### Measurement of the steady-state extensional viscosity of a linear polymer solution using a differential pressure extensional rheometer on a chip

Seo Gyun Kim, Chang Min Ok, and Heon Sang Lee

Department of Chemical Engineering, Dong-A University, Busan, Republic of Korea

The steady-state extensional viscosity in fully developed elongational flow of a semi-dilute poly(ethylene oxide) solution has been evaluated by using a differential pressure extensional rheometer (DPER) on a chip. At low extension rates, the extensional viscosity exhibits strain thinning behavior with a power-law exponent of -0.5. At intermediate extension rates, the extensional viscosity exhibits strain thickening. At high extension rates, the plateau extensional viscosity has been evaluated, and the corresponding finite extendable non-linear elastic (FENE) constant is evaluated to be 45.5 from the experimental results. From the measured normal stress, the extensional relaxation time distribution is also obtained by the inverse calculation using Giesekus-Leonov model.

Monday 2:20 San Felipe Room

ET8

### Liquid-liquid interface capillary breakup extensional rheometry

Christian Clasen<sup>1</sup>, Susanna Formenti<sup>1</sup>, Karel Verbeke<sup>1</sup>, Naveen K. Reddy<sup>2</sup>, Christos Mitrias<sup>3</sup>, Patrick D. Anderson<sup>3</sup>, and Francesco Briatico Vangosa<sup>4</sup>

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Uniaxial extensional rheometry via the capillary breakup of liquid filaments is classically related to liquid-air interfaces as the source for the driving capillary pressure. However, the presence of a surrounding medium of different viscosity and an altered interfacial tension can change the thinning dynamics significantly, so that classical descriptions need to be reconsidered. Pioneering studies focused mainly on selected viscosity ratios of inner to outer fluid and the late-stage thinning close to pinch-off in dripping experiments proposing different similarity solutions for well-defined regimes of the Navier-Stokes equations.

In the current paper we explore the thinning behavior also away from the self-similar final stage of pinch-off and over the full range of available viscosities and viscosity ratios. Capillary thinning of filaments with liquid-liquid interfaces is investigated with a high-resolution optical setup with a novel version of a capillary breakup setup that allows to control the instability wavelengths of filaments in a liquid-in-liquid environment.

The results reveal clear and so far unobserved transitions between thinning regimes for which we present novel criteria based on a non-dimensional analysis. Furthermore, to test the validity of novel transition criteria and to establish their critical values, the whole operating space is experimentally verified with absolute fluid viscosities ranging from  $10^{-5}$  Pas (air) to 5.4 Pas (silicon oil) and thus viscosity ratios from 67407 to  $10^{-4}$  applied in experimental scenarios of gas(-filament)-in-liquid over liquid-in liquid to liquid-in-gas. The experiments are verified with direct numerical simulations using the finite element method. Based on this verification the simulations are subsequently used to complete the parameter space and to explore transition criteria in the experimentally not accessible regimes due to temporal and spatial resolution limits as well as viscosity range limitations of the accessible fluids.

Monday 2:45 San Felipe Room

ET9

**Dielectric RheoSANS: A technique for the simultaneous interrogation of the electrical, mechanical and structure properties of soft matter**

Jeffrey J. Richards<sup>1</sup>, John K. Riley<sup>1</sup>, Paul D. Butler<sup>1</sup>, and Norman J. Wagner<sup>2</sup>

<sup>1</sup>NCNR, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States; <sup>2</sup>University of Delaware, Newark, DE, United States

In situ measurements are an increasingly important tool to inform the complex relationship between nanoscale properties and macroscopic measurements. For soft matter, understanding these relationships provides a pathway to engineer materials with new properties. In order to reveal the relationships that connect the electrical and mechanical properties of colloidal suspensions and self-assembled materials, we have developed a Dielectric RheoSANS sample environment at the NIST Center for Neutron Research. The environment consists of a Couette geometry mounted on an ARES G2 strain controlled rheometer enclosed in a modified Forced Convection Oven (FCO). Inside the Couette, the sample is confined between concentric titanium cylinders that are transparent to neutrons. Both cylinders are electrically isolated from the rheometer. In a Dielectric RheoSANS experiment, the impedance response is measured by an LCR meter and stress response is measured by the torque transducer connected to the inner cylinder. At the same time, small angle neutron scattering measurements (SANS) are made through the radial position of the Couette. By leveraging event mode SANS acquisition and advanced experiment synchronization protocols, we collect the transient electrical and mechanical response of a material as it undergoes a pre-programmed deformation profile at the same time as the transient microstructural response. In this talk, I will highlight several case studies that exemplify the type of transient and steady state experiments that can benefit from the technique.

Monday 3:45 San Felipe Room

Keynote ET10

**Combining time-resolved rheo-SANS and rheo-SAXS to study molecular and crystal alignment of highly-entangled  $\alpha$ -olefin molecular bottlebrushes during uniaxial deformation**

Carlos López-Barrón

*Exxon Mobil Chemical Company, Baytown, TX, United States*

Molecular bottlebrushes are branched polymers with very high graft density which results in very rigid backbones. This conformation provides unique rheological properties compared to linear polymer melts. For instance, their very large entanglement molecular weight ( $M_e$ ) results in very low elastic modulus, which could be used to produce super-soft elastomers [Pakula et al., *Polymer* 47, 7198 (2006)]. Despite the growing interest in bottlebrush polymers, very few studies have been devoted to their linear viscoelastic response, whereas, to our knowledge, no study has been reported on their extensional rheology or their response to cold-drawing. We synthesized a series of ultra-high molecular weight (UHMW)  $\alpha$ -olefin molecular bottlebrushes by organometallic coordinative insertion polymerization of 1-alkenes with lengths ranging from 6 to 18 carbons. The molecular weight of these polymers are in the order of a few million g/mol, which allows accurate measurement of their rubbery plateau modulus ( $G_N$ ) and their  $M_e$  values. The latter is an increasing function of the side chain length ( $N_{sc}$ ) and takes values ranging from 25 kg/mol (for poly(1-octene)) to 115 kg/mol (for poly(1-octadecene)). Therefore, our bottlebrush polymers are highly-entangled and have sufficient melt strength to perform extensional rheology measurements using a commercial Sentmanat extensional rheometer (SER). Bottlebrush chain alignment was measured using a novel method that combines the use of a SER with time-resolved small-angle neutron scattering (SANS) measurements [López-Barrón et al., *J Rheol.* 61, 697 (2017)]. The latter uses state of the art methods of neutron time stamping in the SANS detector and deconvolution protocols that yields scattering data with time resolutions of the order of seconds [López-Barrón et al., *Phys. Rev. Lett.* 108, 258301; Calabrese et al., *Soft Matter* 12, 2301 (2016)]. Those measurements were used to confirm the direct correlation between strain hardening and bottlebrush chain alignment. The latter was quantified using an alignment factor,  $A_f$ , which is correlated with the measured tensile stress. Complementary, in situ wide- and small-angle X-ray scattering measurements reveal that chain alignment is concomitant of self-assembly of the bottlebrush molecules into hexagonal packed cylinder (HEX) phases induced by uniaxial extension. This work reports the first direct evidence of strain-induced alignment and packing of molecular bottlebrushes and their relation with the macroscopic rheological and mechanical responses.

Monday 4:10 San Felipe Room

ET11

**Probing nanostructure under controlled complex deformations with neutron scattering in a fluidic four-roll mill**

Patrick T. Corona<sup>1</sup>, Nino Ruocco<sup>1</sup>, Katie M. Weigandt<sup>2</sup>, L. Gary Leal<sup>1</sup>, and Matthew E. Helgeson<sup>1</sup>

<sup>1</sup>University of California, Santa Barbara, Santa Barbara, CA 93106, United States; <sup>2</sup>Center for Neutron Research, NIST, Gaithersburg, MD 20899, United States

Industrial processing of complex fluids involves a wide range of flow histories that change the material's nanostructure and, therefore, the properties of the final product. Current means for measuring flow-induced nanostructure have focused primarily on measurements in purely

shearing or extensional deformations, which fail to capture the highly nonlinear behavior of soft materials under more realistic flows. To overcome this limitation, we have developed a new fluidic four roll mill (FFoRM) device for measurements of flow-induced structural changes in variable, near-2D deformation fields. The device, based on a previously designed fluidic four-roll mill, has been modified to produce well-controlled, uniform flows for in situ small-angle neutron scattering (SANS) measurements on fluids with a range of rheological responses including shear thinning and thickening, as well as viscoelasticity and yield stresses. As a test of these capabilities, we apply SANS in the FFoRM to characterize the non-equilibrium microstructure of a dispersion of cellulose nanocrystals (CNC) in flows with a range of deformation types. Particle tracking velocimetry verifies the ability to produce flow fields of arbitrary deformation type in these dispersions. Subsequent FFoRM-SANS measurements are combined with scattering models for oriented particles to determine the orientation distribution of the dispersion over a wide range of deformation types and rates. The results are consistent with a rheological model for semi-dilute colloidal rod dispersions, verifying the ability of FFoRM-SANS to characterize the flow-induced microstructure of complex fluids in response to a range of programmable deformations.

Monday 4:35 San Felipe Room

ET12

### **Simultaneous slit rheology and structural characterization with small angle neutron scattering**

Katie M. Weigandt<sup>1</sup>, Javen Weston<sup>2</sup>, and Steven Hudson<sup>3</sup>

<sup>1</sup>Center for Neutron Research, NIST, Gaithersburg, MD 20899, United States; <sup>2</sup>Chemical Engineering, University of Tulsa, Tulsa, OK 74104, United States; <sup>3</sup>Polymers and Complex Fluids Group, NIST, Gaithersburg, MD 20899, United States

We are developing slit rheometers compatible with simultaneous small angle neutron scattering (SANS) measurements to directly correlate structure and rheology over a broad range of conditions. Eventually we hope to probe sample structure in Poiseuille flow at high shear rates, under high pressure head, and relatively high temperatures. This builds upon an existing suite of Couette rheoSANS and flowSANS devices at the NIST Center for Neutron Research that are accessible to the scientific community through a peer reviewed proposal system. Industrial applications, such as lubrication, mixing, spraying and injection, involve the flow of complex fluids at high deformation rates. Clogging, fluid degradation, and other processing challenges can arise in these extreme contexts and are often driven by structural changes in the fluid. To date, we have developed a prototype slit rheometer capable of simultaneously measuring structure and rheology of relatively low viscosity or shear thinning fluids ( $\eta < 5$  mPa·s) at shear rates up to 100,000 s<sup>-1</sup>. Our initial investigations have focused on measuring wormlike micelle solutions at low to moderate shear rates and comparing the results with Couette rheoSANS measurements. In this talk we will discuss the ongoing development of  $\mu$ RheoSANS measurements including our existing low-pressure apparatus and our newly built high pressure  $\mu$ RheoSANS device, designed to withstand pressure drops or pressure heads up to 350 bar. This device will enable us to measure SANS at shear rates up to 10<sup>6</sup> in samples with  $\eta \sim 100$  mPa·s.

Monday 5:00 San Felipe Room

ET13

### **Elastic particle deformation in rectangular channel flow as a measure of particle stiffness**

Margaret Y. Hwang<sup>1</sup>, Seo Gyun Kim<sup>2</sup>, Heon Sang Lee<sup>2</sup>, and Susan J. Muller<sup>1</sup>

<sup>1</sup>Chemical & Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, United States; <sup>2</sup>Department of Chemical Engineering, Dong-A University, Busan, Republic of Korea

We synthesized, characterized, and measured the deformation of soft elastic microparticles in flow in a microchannel. Lightly crosslinked microparticles of pNIPAM were synthesized in a modified microfluidic flow focusing device. By varying the concentration of crosslinker, two sets of particles with different properties were produced. Capillary micromechanics measurements identified the shear moduli of the two sets as 13.3 Pa and 32.5 Pa and the compressive moduli as 66 Pa and 79 Pa, respectively. The flow of these particles in confined flow in microchannels of rectangular cross-section was then observed as a function of flow rate. Under flow, the particle shapes transitioned from circular to egg-shaped, triangular, arrowhead, and ultimately parachute shaped with increasing shear rate. Several of these observed shapes were distinct from those previously reported in the literature for vesicles and capsules. Shape changes were reversible, and deformed particles relaxed back to circular/spherical in the absence of flow. The thresholds for shape transitions were quantified using a non-dimensional radius of curvature at the tip, particle deformation, circularity, and the depth of the concave dimple at the trailing edge. Due to variations in the shear moduli between particles within a batch of particles, each flow rate corresponded to a small but finite range of capillary number (Ca) and resulted in a series of shapes. By arranging the images on a plot of Ca versus circularity, a direct correlation was developed between shape and Ca and thus between particle deformation and shear modulus. As the shape was very sensitive to differences in shear modulus, particle deformation in confined channel flow may allow for better differentiation of microparticle shear modulus than other methods.

## Symposium BA Biological and Active Matters

Organizers: Pushkar Lele and Kelly Schulz

Monday 1:30 Tanglewood

BA6

### **Effect of surfactant size on the development of pellicles**

Lingjuan Qi and Gordon F. Christopher

*Texas Tech Univ, Lubbock, TX 79423, United States*

Pellicles, bacterial communities at a liquid interface surrounded by self-secreted extracellular polymer matrix, are found in all manner of environments including human hosted infections, aquatic ecosystems, and industrial equipment. Although biofilms at solid surfaces have been widely studied, pellicle development and the role of the interface on development have not been well characterized. To enable such studies, interfacial rheology can be used as an effective tool to monitor the various stage of pellicle growth. Using this technique, we have previously shown that traditional means of bio attachment are unnecessary for pellicle growth due to surface tension mediated attachment. In this work we continue to explore the role of surface tension by using  $C_xE_y$  surfactants to modify the liquid interface in a controlled manner.

Surfactants with a range of head and tail sizes were added to bacteria either during inoculation, at the start of pellicle growth, or after pellicle formation had occurred. In all cases where surfactant was added before pellicles were observed, surfactant acted to delay pellicle growth; the extent of the delay was loosely tied to the surfactant tail size. To better understand the mechanism of the delay, contact angle of water on bacteria/surfactant mixtures was measured for both biofilms as well as hydrated bacteria lawns. This contact angle measurements are compared to pellicle growth and rheology. These results confirm the importance of the surface tension as a primary means of attachment for pellicle growth and point to methods to modify pellicle formation in a controlled manner.

Monday 1:55 Tanglewood

BA7

### **Characterization of dual-species biofilm of *Bacillus licheniformis* and *Pseudomonas fluorescens* at the air-liquid interface**

Clémence Abriat<sup>1</sup>, Marie-Claude Heuzey<sup>1</sup>, Nick Virgilio<sup>1</sup>, and France Daigle<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Polytechnique Montreal, Montreal, Quebec, Canada;* <sup>2</sup>*Département de microbiologie, infectiologie et immunologie, Université de Montreal, Montreal, Canada*

Biofilms are complex structures comprising bacteria cells embedded in an extracellular matrix (ECM) composed of polymeric substances secreted by the bacteria. They are associated with biofouling, food and water contamination, and bacterial infections resulting in both significant economic and human costs. Biofilms can be located at the air-liquid interface, in which case they are called pellicles. Better characterization and understanding of the ECM properties are required if we want to ultimately control or inhibit their growth. Interfacial shear rheology is a unique technique to quantify a biofilm's mechanical properties at the air/liquid interface in real time. To bring a new understanding on how the interactions between bacteria affect the mechanical properties of biofilm, we investigated a biofilm composed of two bacteria commonly found in multiple food contamination and food poisoning cases: *Bacillus licheniformis* and *Pseudomonas fluorescens*. We measured the viscoelastic growth profile of the model dual-species biofilm during its formation and quantified the biofilm mechanical properties at the air-liquid interface. Different bacteria ratios were tested to probe the interactions among bacteria. To complement the quantitative rheology information showing antagonistic interactions in our model system, microbiology experiments - such as determination of the biomass, viability bacterial counts and fluorescence microscopic analysis - were performed. The sensitivity of one bacteria to the other was evaluated during planktonic growth and the results linked the influence of growth kinetics to the final composition of the dual-species biofilm, validating the hypothesis formulated with the rheological quantitative information. Altogether, we were able to relate the unique changes in viscosity and elasticity of the dual-species biofilm to bacterial growth, providing fundamental knowledge required to biofilm removal.

Monday 2:20 Tanglewood

BA8

### **Viscosity of confined bacterial suspensions**

Zhengyang Liu<sup>1</sup>, Shweta Narayan<sup>2</sup>, Cari S. Dutcher<sup>2</sup>, Kechun Zhang<sup>1</sup>, and Xiang Cheng<sup>1</sup>

<sup>1</sup>*Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States;* <sup>2</sup>*Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States*

Bacterial suspensions, a premier example of active fluids, show reduced viscosity compared to their counterpart colloidal suspensions. Bacterial "superfluid" with zero apparent viscosity has been shown in both bulk rheological measurements and bacterial "racetrack" experiments under strong confinement. These experiments suggest that geometry, in particular confinement, of systems plays an important role in modifying the viscosity of bacterial suspensions. Here, by adapting a microfluidic viscometer, we investigate the viscosity of bacterial suspensions in different confined geometries. We identified a strong confinement effect when the confinement length scale is below 50 microns, where the viscosity of bacterial suspensions decreases by a factor of 2.5, when the confinement decreases from 50 microns down to 25 microns. Above 50 microns, the viscosity of bacterial suspensions saturates and is independent of confinement. We further confirmed the result with a droplet based viscometer.

Monday 2:45 Tanglewood

BA9

**Symmetric shear banding and swarming vortices in bacterial “superfluids”**Xiang Cheng<sup>1</sup>, Shuo Guo<sup>1</sup>, Devranjan Samanta<sup>2</sup>, Yi Peng<sup>1</sup>, and Xinliang Xu<sup>3</sup><sup>1</sup>*Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States;* <sup>2</sup>*Mechanical Engineering, Indian Institute of Technology, Ropar, Ropar, India;* <sup>3</sup>*Beijing Computational Science Research Center, Beijing, China*

Bacterial suspensions can flow without apparent viscosity. Such a superfluid-like behavior stems from the collective motions of swimming bacteria. Here, we explore the microscopic flow profile of bacterial “superfluids” under simple shear. We find that, instead of deforming uniformly, bacterial “superfluids” develop multiple shear bands, i.e., regions with different shear deformations. We construct a simple model that quantitatively describes the shape of the shear-banding structure and reveals important physical properties of collective bacterial motions. Our study sheds light on complex interactions between swimming microorganisms and ambient fluid flows, crucial for the survival of microorganisms in nature and the manipulation of bacterial suspensions in engineering settings.

Monday 3:45 Tanglewood

BA10

**Controlling the microscopic dynamics and rheology of colloidal gels with active motion**Megan E. Szakasits<sup>1</sup>, Keara T. Saud<sup>2</sup>, and Michael J. Solomon<sup>1</sup><sup>1</sup>*Chemical Engineering, University of Michigan, Ann Arbor, MI 48105, United States;* <sup>2</sup>*Materials Science and Engineering, University of Michigan, Ann Arbor, MI, United States*

Colloidal gels are a state of soft matter with attractively bonded particles in a network. These materials have important rheological properties, such as linear elasticity and a yield stress. Here, we embed active particles in colloidal gel networks to tune the microscopic dynamics and rheology of the gel network. We activate the embedded active colloids through addition of hydrogen peroxide and characterize the dynamics and rheology of the gel network as a function of the hydrogen peroxide concentration - a fuel that drives diffusiophoretic motion of the active colloids. Active motion enhances the dynamics of the gel network, and the amount of enhancement is a function of the inputted active energy. We find that the enhancement in gel dynamics is strongly correlated with changes in the elastic modulus of the gel network. Our results demonstrate how the mechanical properties of gel networks can be tuned through varying the concentration of active particles and hydrogen peroxide concentration. Through addition and depletion of the active component, we can create gels with multi-state mechanical properties, which is useful for the industrial applications of gels such as paints and coatings, consumer products and agricultural formulations.

Monday 4:10 Tanglewood

BA11

**Scaling theory for athermal fiber networks**Jordan Shivers<sup>1</sup>, Sadjad Arzash<sup>1</sup>, Abhinav Sharma<sup>2</sup>, and Fred C. MacKintosh<sup>1</sup><sup>1</sup>*Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States;* <sup>2</sup>*Leibniz Institute for Polymer Research, Dresden 01069, Germany*

Networks of interconnected semiflexible fibers, such as the cell cytoskeleton and extracellular matrix in living tissues, provide structural integrity and mechanical tunability to many natural materials. Whether the mechanical response of these networks is dominated by soft bending modes or stiff stretching modes can be controlled by two variables: the coordination number and the applied strain. Near the transition between soft and rigid, such networks exhibit signatures of criticality in the strain- and connectivity-dependence of the stress tensor, elastic moduli and nonaffine rearrangements. We develop a scaling theory describing the rigidity transition for athermal fiber networks and determine relations between the various critical exponents, which we support with simulations of lattice-based and off-lattice fiber networks.

Monday 4:35 Tanglewood

BA12

**Competition between motor and Brownian forces in active gels**Andrés Córdoba*Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile*

Active gels perform key mechanical roles inside the cell, such as cell division, motion and force sensing. The unique mechanical properties required to perform such functions arise from the interactions between molecular motors and semi-flexible polymeric filaments. Molecular motors can convert the energy released in the hydrolysis of ATP into forces of up to pico-Newton magnitudes. Moreover, the polymeric filaments that form active gels are flexible enough to respond to Brownian forces, but also stiff enough to support the large tensions induced by the motor-generated forces. Here, a microscopic mean-field theory of active gels originally formulated in the limit of motor-dominated dynamics is extended to include Brownian forces. It is shown that a subtle interplay, or competition, between motor-generated forces and Brownian forces has an important impact in the mass transport and rheological properties of active gels. The model predictions show that at low frequencies the dynamic modulus of active gels is determined mostly by motor protein dynamics. However, Brownian forces significantly increase the breadth of the relaxation spectrum and can affect the shape of the dynamic modulus over a wide frequency range even for ratios of motor to Brownian forces of more than a hundred. Moreover, for ratios between motor and Brownian forces of up to a thousand the results show that up to eight percent of additional buckling of the polymeric filaments can be caused by the presence of Brownian forces. Since the ratio between motor and Brownian forces is sensitive to ATP concentration, the results presented here shed some light on how the transient mechanical response of active gels changes with varying ATP concentration.

Monday 5:00 Tanglewood

BA13

**Fundamental principles behind the emergence of contractility in acto-myosin networks**Garegin Papoian*University of Maryland, College Park, MD 20817, United States*

We investigate the emergence of contractile behaviors in disordered non-muscle actomyosin networks, whose non-equilibrium dynamics remain largely unexplored when containing reversibly-bound passive cross-linkers and active myosin II motor filaments. Current understanding of how contractility emerges in disordered actomyosin networks of non-muscle cells is still largely based on the intuition derived from earlier works on muscle contractility. In this work, we show that fundamental contractile elements in actomyosin networks, called force dipoles, harness the thermodynamic free energy of an auxiliary cross-linking protein binding, independent of motor processes. Surprisingly, we discovered that both energy- and non-energy-consuming proteins in tandem can greatly amplify forces at a microscopic level, due to a structural ratcheting of the motor by cross-linking proteins. Our work explains this synergistic phenomenon and provides scaling laws for how this force generation depends on the thermodynamic properties of the proteins, pointing to a non-equilibrium ratcheting mechanism as an important requirement for significant contractile force generation in non-muscle actomyosin systems. These findings begin to elucidate the tools available to this biological active matter to dramatically alter their micro-structural morphologies and generate active cellular forces in response to external chemical signaling and mechanical cues.

**Symposium FP****Food, Pharmaceuticals & Cosmetics**

Organizers: Siva A. Vanapalli and Michael Boehm

Monday 1:30 Plaza II

Keynote.....FP6

**Creating stable colloidal systems using insoluble fiber networks**Ross Clark*San Diego R&D, CP Kelco, San Diego, CA 92123, United States*

Nearly all foods, household products and personal care items require some form of colloidal stabilization. Whether it is oil in a salad dressing or abrasive in a cleaner, good long term stability of dispersed phase particles is needed. Most often stabilization is achieved using water soluble polymers that increase aqueous phase viscosity. Water soluble polymers provide properties such as relatively high elastic modulus or yield stress values that restrict the movement of the dispersed phase while still allowing the product to pour, pump and spread.

As good as these water soluble polymers are, some manufacturers seek alternatives due to consumer preferences for features such as natural, non-GMO or organic. There are also cases where water soluble polymers can degrade and so fail to provide the needed degree of stability.

These factors create an opportunity to provide colloidal stabilization using novel natural ingredients. An insoluble fiber network can stabilize these difficult systems. One possibility is citrus fiber that has been processed to increase its internal surface area and preserve the natural pectin content. The presence of native pectin provides a co-agent function for the cellulose. Co-agents inhibit the natural tendency of cellulose to self associate with consequent reduction in fiber surface area.

Using an insoluble fiber network requires activation; a process of expanding the processed citrus fiber once it is added to an aqueous system. Activation is different from water soluble polymer hydration; it involves physical separation of the fibers into a reticulated network. Good activation is achieved by applying extensional stresses (aka "high shear mixing") to the dispersion of fiber in water.

Examples of how citrus fiber stabilizes colloids are shown as are bulk rheological and micro-rheology differences that occur with the use of citrus fiber. Challenges and advantages of these systems are discussed.

Monday 1:55 Plaza II

FP7

**Modeling the effects of fat type and crystallization conditions on the wear behaviors of solid fats**Juzhong Tan and Helen S. Joyner*Food Science, University of Idaho, Moscow, ID 83844-2312, United States*

Lipids are major component in many food products such as chocolate, butter and dairy spreads, and ice cream. These lipids have significant the processing properties of food products. Wear behaviors may be a good indication of their ability to undergo processing steps (shredding, shearing, extruding, cutting). Because solid fat wear behaviors are currently unknown, the objective of this study was to develop a numerical model to characterize the wear behavior of solid fats with different crystal microstructures. The wear behaviors of three different fats (cocoa butter, anhydrous milk fat (AMF), and palm oil) crystallized at different temperatures (5-20°C) and cooling rates (0.1°C/min and 5°C/min) were evaluated. Wear behaviors of the three solid fats were evaluated under several normal forces (0.3-2.0N) at room temperature (20±2°C) by a twin-ball-on-disk geometry. A numerical model for penetration depth that accounted for both deformation and wear was developed. All models had mean absolute error <267 μm, indicating good fit. Cocoa butter crystallized at high temperature under slow cooling had higher wear rates and were easier to deform, which was attributed to the transition from a single triacylglyceride crystal form (type V) to the coexistence of various triacylglyceride polymorphs (type I-IV). AMF and palm oil samples crystallized at low temperature under fast cooling showed slower wear rates; these results were due to a decreased number of crystals and increased crystal size. Furthermore, the decrease of the solid fat fraction due in slow-cooled samples also contributed to increased deformation and wear rates. The findings of this study indicate the potential to use tribometry to study solid fat



functional behaviors. Tribometry may also be able to indicate fat processing ability and texture, so this information can be used by food manufacturers for targeted design of fat-based foods.

Monday 2:20 Plaza II

FP8

### **Micromechanical characterization of edible capsules with finite shell thickness**

Abhijeet Kamble<sup>1</sup>, April Xu<sup>1</sup>, Mariano Michelin<sup>2</sup>, Bruna C. Leopércio<sup>2</sup>, Marcio S. Carvalho<sup>2</sup>, and John M. Frostad<sup>1</sup>

<sup>1</sup>University of British Columbia, Vancouver, Canada; <sup>2</sup>Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451900, Brazil

A Cantilevered-Capillary Force Apparatus is a recently developed device that can be used to characterize the mechanical properties of micron-sized capsules. Capsules of this size are a novel material that can be used to create new functional food products and impart novel properties to consumer products. In this study, capsules are produced using a recently developed, flow-based method and are composed of a sunflower-oil core surrounded by a gellan-gum shell. Measurements under quasi-static conditions suggest that the capsules behave as an elastic material that can undergo plastic deformation. Details of the characterization methodology are presented and the effective elastic modulus and onset of plastic deformation is compared for capsules of varying size, shell thickness, and shell composition.

Monday 2:45 Plaza II

FP9

### **Rheology and molecular interactions in therapeutic protein solutions**

Eric M. Furst<sup>1</sup> and Mahlet A. Woldeyes<sup>2</sup>

<sup>1</sup>Dept. of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; <sup>2</sup>University of Delaware, Newark, DE, United States

Improvements in genetic engineering, development, processing, and manufacturing of biotherapeutics have made monoclonal antibodies (mAbs) a leading source of new pharmaceuticals. Currently, there are more than 30 mAbs in clinical trials for autoimmune, oncology, or chronic inflammatory indications. Solution rheology is a key physical property that is often screened during early development and late stage discovery, since downstream processing and manufacturing steps (filtration, pumping, and filling), as well as final administration (including “syringibility”), are substantially affected by the solution viscosity. In this talk, I will focus on the relationship between antibody solution viscosity and molecular interactions of mono- and bispecific molecules. Viscosity and protein interactions are measured using multiple particle tracking (MPT) microrheology and light scattering (LS), respectively. The concentration-, temperature-, and composition-dependence of the solution viscosities will be discussed. The surprising complexity and challenge of establishing clear relations between protein interactions and rheology makes this a rich area for further experimental, theoretical, and computational work.

Monday 3:45 Plaza II

FP10

### **eCapillary: A disposable microfluidic extensional viscometer**

Naureen S. Suteria<sup>1</sup>, Stefan Baier<sup>2</sup>, and Siva A. Vanapalli<sup>1</sup>

<sup>1</sup>Texas Tech University, Lubbock, TX, United States; <sup>2</sup>PepsiCo., Hawthorne, NY 10532, United States

Biofluids (i.e. saliva, etc) are complex viscoelastic fluids whose extensional behavior can be an indicator of a person's health and affect their perception of a consumed beverage. Microfluidics provides an ideal platform to study the extensional behavior of viscoelastic fluids since it allows for high deformation rates while having a low Reynold's number. In this study, we developed the “eCapillary” disposable microfluidic extensional viscometer, which is a portable and disposable device suitable for viscoelastic fluids and biofluids. The technique involves driving the fluid at a constant pressure and measuring the flow rate by using a smartphone to track the fluid interface in the capillary channel. Using the fluid's shear rheology and computational fluid dynamics simulations, we are able to determine the extensional viscosity vs. strain rate of polymeric solutions. We also use dripping-on-substrate rheology to measure the fluid's relaxation time as well as the relaxation time vs. Hencky strain. From our experiments on poly(ethylene oxide) and polyacrylamide, we observe an onset of extensional-thickening behavior at  $De \sim 1$  and the apparently extensional viscosities are orders of magnitude higher than the shear viscosities, illustrating significant impact extensional properties have on a fluid's behavior.

Monday 4:10 Plaza II

FP11

### **Production of monodispersed microcapsules for food applications using microfluidics**

Mariano Michelin<sup>1</sup>, Bruna C. Leopércio<sup>1</sup>, and Marcio S. Carvalho<sup>2</sup>

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Biopolymer-based microcapsules are highly hierarchized structures containing an inner phase and a hydrogel shell. These microcapsules have gained considerable attention in the food industry due to their capacity to improve ingredient handling, to mask any undesirable flavors, or to protect different ingredients from chemical or physical degradation during storage or after ingestion. Biopolymer-based microcapsules can be obtained through external gelation of the middle phase - composed of an aqueous-based biopolymer - of an oil-in-water-in-oil double emulsion template (O/W/O). However, the preparation of O/W/O templates by conventional methods is not trivial and, in general, require two emulsification steps. To overcome this drawback, we used glass-capillary microfluidic device, which combines co-flow and flow-focusing in coaxial glass-capillaries, to produce double emulsion templates of microcapsules. The innermost, middle and continuous phases were composed by sunflower oil, low acyl gellan gum (0.5% wt) and Tween20 (2.0% wt), sunflower oil dispersion containing calcium acetate (1.0% wt) and polyglycerol-

polyricinoleate (5.0% wt), respectively. We determined the range of flow rates that led to the desired intermittent and continuous dripping flow regime and how the microcapsule diameter and shell thickness changed with flow conditions. We produced microcapsules using FDA-approved ingredients with diameters from 130 to 260  $\mu\text{m}$  and shell thickness varying from 3 to 20  $\mu\text{m}$ .

Monday 4:35 Plaza II

FP12

### **Investigating cocoa butter polymorph formation through in situ rheology and Raman spectroscopy**

Nathan C. Crawford, Mohammed Ibrahim, and Rui Chen

*Thermo Fisher Scientific, Madison, WI 53711, United States*

Rheology coupled with *in situ* Raman spectroscopy (rheoRaman) was used to examine the isothermal crystallization of cocoa butter (CB). Two unique isolation protocols were employed to form cocoa butter polymorphs Form III and Form IV. As CB transitioned from the amorphous to the crystalline state, significant Raman spectral changes in the C-H stretching region (2700-3050  $\text{cm}^{-1}$ ), the C-C stretching region (1000-1200  $\text{cm}^{-1}$ ), and the  $\text{CH}_2$  twisting region (1250-1300  $\text{cm}^{-1}$ ) were observed. The  $\nu_s(\text{CH}_2)$  mode at 2850  $\text{cm}^{-1}$  was dominant in the liquid phase (or melt state), whereas the  $\nu_{\text{as}}(\text{CH}_2)$  mode at 2882  $\text{cm}^{-1}$  and the  $\nu_s(\text{C-C})$  mode at 1130  $\text{cm}^{-1}$  were prominent in the solid state (or crystalline phase).

For the formation of CB polymorph Form III, the rheological response (elastic modulus  $G'$  and viscous modulus  $G''$  vs. time) was directly correlated with the spectral marker profiles (peak ratio vs. time), suggesting that the bulk hardening of CB and the formation of crystalline structures occurred simultaneously. In contrast, for CB polymorph Form IV, there was a noticeable time lag between the rheological response ( $G'$  and  $G''$ ) and the Raman spectral profiles. The observed time delay indicates that CB polymorph Form IV crystallized by first hardening into an amorphous solid, manifested by a sharp increase in  $G'$  and  $G''$  while the Raman features remained unchanged. The amorphous solid then underwent a morphological transition to form a crystalline solid, signified by the increase in Raman features associated with crystal CB structures (1130 and 2882  $\text{cm}^{-1}$ ). Overall, the hyphenation of these two independent analytical techniques, rheology and Raman spectroscopy, enabled a more holistic depiction of the crystallization process and provided unique insights into the formation of CB polymorph Forms III and IV.

Monday 5:00 Plaza II

FP13

### **Fourier transform rheology of acrylate copolymer dispersion in thermoplastic elastomer**

Mariko Hasebe, Norbert Biderman, and Hy Bui

*L'Oreal, Clark, NJ, United States*

Thermoplastic Elastomers (TPE) are copolymers that form physically cross-linked networks through micro-phase separation, and exhibit both thermoplastic and elastic properties. One interesting thermoplastic elastomer that is widely used in shoe soles and pressure sensitive adhesives is Styrene-butadiene-Styrene block copolymer, also known as Kraton polymer. This Styrene type TPE has been employed for cosmetic applications as an oil-phase gelling agent in anhydrous products as an alternative to organo-clays and fumed silica. This talk will focus on the association of Kraton SEBS (Styrene-Ethylene/Butylene-Styrene) copolymer with a Non-Aqueous Dispersion (NAD) of acrylates/isobornyl acrylate copolymer in a volatile solvent at various blend ratios. The non-linear rheology using Fourier transform will be used to understand the effect of mixing these two materials into final microstructures. We observed that upon mixing, the non-aqueous dispersion of acrylate copolymers aggregated into separate domains in thermoplastic elastomer.

## Tuesday Morning

### Symposium PL Plenary Lectures

#### *Bingham Lecture*

Tuesday 8:30 Galleria I

PL2

#### **Rheology of ring polymer melts**

Michael Rubinstein<sup>1</sup>, Ting Ge<sup>1</sup>, Sergey Panyukov<sup>2</sup>, Gary S. Grest<sup>3</sup>, and Dimitris Vlassopoulos<sup>4</sup>

<sup>1</sup>*Mechanical Engineering and Materials Science, Duke University, Durham, NC 27710, United States;* <sup>2</sup>*Russian Academy of Sciences, Moscow, Russia;* <sup>3</sup>*Sandia National Laboratories, Albuquerque, NM 87185, United States;* <sup>4</sup>*Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece*

Some of the most interesting rheological features of polymer solutions and melts are due to entanglements between macromolecules. Entanglements between linear polymers as well as between branched polymers strongly affect dynamical properties of these materials, but do not affect equilibrium conformations of these molecules. A unique feature of cyclic polymers (rings) is that entanglements affect both their rheology and conformations. Topological interactions due to the non-concatenation condition compress ring molecules into fractal globules and force them to stay at marginal overlap with each other. Stress relaxation function of melts of ring polymers is a power law function of time without a rubbery plateau, reflecting unique self-similar dynamics of these molecules on different length and times scales. We introduce nanorheology as a method of obtaining relaxation modes of a polymer matrix from the mean square displacement of non-sticky nanoparticles and discuss the dependence of nanoparticle size on the modes obtained by this method for both linear and ring polymer melts. Mixing non-sticky nanoparticles with polymers can either increase or decrease the viscosity of this nanocomposite with respect to the viscosity of pure polymer melt. Shear rate dependence of viscosity of ring polymers is qualitatively different from shear thinning of linear polymers due to the absence of long-lived entanglements in ring polymer melts. Application of unique entanglement features of ring polymers to the elasticity of polymer networks and nuclear physics will be discussed.

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Tuesday 9:50 Galleria I

SC14

#### **Thermal processing of colloidal gels: Kinetics of quenching, coarsening and arrest**

Matthew E. Helgeson<sup>1</sup>, Tuan Nguyen<sup>1</sup>, Poornima Padmanabhan<sup>2</sup>, and Roseanna N. Zia<sup>3</sup>

<sup>1</sup>*University of California, Santa Barbara, Santa Barbara, CA 93106, United States;* <sup>2</sup>*Rochester Institute of Technology, Rochester, NY, United States;* <sup>3</sup>*Chemical Engineering, Stanford University, Stanford, CA, CA 94305-4125, United States*

Colloidal suspensions exhibiting thermoresponsive interparticle attractions have opened up a vast new design space for the thermal processing of colloidal gels and glasses akin to centuries-old strategies in atomic and molecular materials, in which the controlled initiation and quenched arrest of phase instability can be used to tailor material properties. Here, we present initial steps toward exploring this space via a combination of experiments and large-scale dynamic simulations. Experiments comprise model colloidal suspensions containing thermoreversible bridging polymers which exhibit gelation concomitant with arrested phase separation by spinodal decomposition. The system is translated to detailed, parameter-matched dynamic simulations, where measurements of particle-level structure and dynamics provide complementary insights to experimental observations. Upon establishing the equilibrium fluid-fluid phase coexistence and non-equilibrium attractive glass transition for the system, we systematically study how the kinetics of spinodal coarsening and gelation depend on the details of the thermal quench taken - i.e., the depth and rate of temperature change into the arrested state within the region of phase coexistence. To demonstrate the utility of thermal processing, we show how these quench/anneal protocols can be used to modulate the linear and nonlinear rheological properties of arrested colloidal gels.

Tuesday 10:15 Galleria I

SC15

#### **Flow and structure during drying of colloid-polymer thin films**

James F. Gilchrist<sup>1</sup> and Thitiporn Kaewpetch<sup>2</sup>

<sup>1</sup>*Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA, United States;* <sup>2</sup>*Polymer Science and Engineering, Lehigh University, Bethlehem, PA, United States*

Drying process is essential to various industrial applications including pharmaceutical drug-release films for dermal and oral drug delivery. One of the primary concerns is the distribution of active ingredients within dry films. In colloid-polymer mixtures, the drying mechanism is complicated

and its study is limited. Prior studies show the drying behavior of the colloid-polymer mixtures at various pH, including particle dispersion and flocculation due to depletion interactions between colloidal particles and non-adsorbing polymers by using small-angle X-ray scattering and stress development. This work is an experimental in-situ investigation of the drying mechanism and film formation of colloid-polymer mixtures using confocal laser scanning microscopy to visualize the internal structural evolution of surrogate “active” ingredients. The mixtures prepared at high and low pH start as colloidal liquids or gels and are investigated over various colloid and polymer concentrations. Suspensions are drawn into thin films on glass substrates and dried at room temperature. During drying process, the film is evaluated by monitoring the dynamic evolution of the distribution and 3D structure of colloidal particles by analyzing the concentration profile, the number of nearest neighbors, the radial distribution function, and the Voronoi polyhedra distributions. In between these 3D scans, 2D scanning to determine the microrheology and internal flow is also obtained. The concentration and gel formation lead to the differences in particle distribution of the dry films. In gel samples, the time evolution of the structure is highly complex, sometimes experiencing periodic gel formation, gel breaking, flow and restructuring before the final structure is permanently immobilized. Moreover, the particle aggregation between liquid and gel mixtures during drying shows distinguishing patterns which are more comprehensible and useful for the industrial process and determining the final structure that dictates drug delivery.

Tuesday 10:40 Galleria I

SC16

### **Rheological properties of aqueous suspensions of cellulose nanocrystals modified by polyethyleneimine**

Dhriti Khandal, Jason R. Tavares, Marie-Claude Heuzey, and Pierre J. Carreau

*Crepec, Chemical Engineering, Polytechnique Montreal, Montreal, QC H3C3A7, Canada*

Cellulose nanocrystals (CNCs) have potential for commercial applications in different fields ranging from the development of dispersions with interesting rheological properties, to reinforcing polymers, or creating novel materials with specific optical properties. In this work we have examined the rheological properties of aqueous suspensions of CNCs modified by polyethyleneimine (PEI), a water soluble cationic synthetic polymer that is often used in biomedical applications for its amine functionalities and anti-microbial properties. The use of PEI has also been reported as a low toxicity crosslinker in cellulose nanofibrils (CNFs)[1-3]. The Newtonian 3% (w/w) aqueous CNC suspensions were found to develop into a gel system after modification with as low as 0.01 g eq of PEI per g of CNC in the suspension. An increase of almost 3 decades in the complex viscosity was observed during the evolution of the freshly prepared 3% (w/w) CNC-PEI suspensions into a gel. The viscoelastic gel formed for different compositions of CNC-PEI has been studied under both linear and non-linear domains of viscoelasticity. It was found that such gels had a tendency to gradually re-form after shear deformation. The morphology and surface modification of CNCs by PEI was uniform and analyzed by other techniques, such as transmission electron microscope (TEM), X-ray spectrophotometry (XPS), and elemental analysis.

References: [1] Reddy B.R., Eoff L., Dalrymple E.D., Black K., Brown D., Rietjens M., A Natural Polymer-Based Cross-Linker System for Conformance Gel Systems, Society of Petroleum Engineers, 2003, 8, 99-103. [2] Syverud K, Kirsebom H, Hajizadeh S, Chinga-Carrasco G, Cross-linking cellulose nanofibrils for potential elastic cryo-structured gels, *Nanoscale Res Lett*, 2011, 6:626, 1-6. [3] Alexandrescu L., Syverud K., Gatti A., Chinga-Carrasco G., Cytotoxicity tests of cellulose nanofibril-based structures, *Cellulose*, 2013, 20, 1765-1775.

Tuesday 11:05 Galleria I

SC17

### **Shear-induced microstructural gradients in colloidal gels for composite hydrogel fibers**

E. Daniel Cardenas-Vasquez and Lilian C. Hsiao

*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States*

Thermoresponsive nanoemulsions that contain a bridging polymer are known to self-assemble into colloidal gel structures above the critical gel temperature. We incorporate thermoresponsive nanoemulsions into composite hydrogels fibers by using ultraviolet (UV) light to photopolymerize the liquid precursor in a continuous process. The oil-in-water nanoemulsions consist of fluorescently dyed poly(dimethyl siloxane) (PDMS) droplets (droplet size  $2a = 40\text{nm}$ , volume fraction  $f = 0.2$ ) suspended in a continuous phase of poly(ethylene glycol) diacrylate as the crosslinker and sodium dodecyl sulfate as the surfactant. Steady shear experiments of the precursor show a shear thinning behavior at temperatures higher than the gel point, and temperature ramp rheology (rate =  $1^\circ\text{C}/\text{min}$ ) performed on the precursor shows that the gelation temperature is  $T_{\text{gel}} = 29^\circ\text{C}$ . We tune the precursor flow rate (0.2-0.9 mL/min) as well as the precursor temperatures ( $22^\circ\text{C} = T = 40^\circ\text{C}$ ) to obtain photopolymerized hydrogel fibers with various microstructures. A velocity profile of the precursor flow in the channel, obtained by solving the Navier-Stokes equations for a yield stress fluid, suggests that the spatial variations in microstructure within the fibers may arise due to selective yielding of the colloidal gels during shear. Using this method, we synthesize composite hydrogel fibers with a variety of microstructural gradients in the velocity gradient direction of flow. The characteristic length scales of the colloidal microstructure are quantified using confocal microscopy and cryogenic scanning electron microscopy. The results show that local gradients in shear flow could be used to deliberately introduce microstructural variations in the manufacturing of composite soft materials, with applications such as hydrogel membranes, microfluidic platforms, and functional fibers.

Tuesday 11:30 Galleria I

SC18

### **Telechelic Star Polymers as models for soft-patchy colloids with tunable rheology**

Esmael Moghimi<sup>1</sup>, Dimitris Vlassopoulos<sup>2</sup>, Christos N. Likos<sup>3</sup>, and Nikos Hadjichristidis<sup>4</sup>

<sup>1</sup>*FORTH-IESL, Heraklion, Greece;* <sup>2</sup>*Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece;* <sup>3</sup>*Faculty of Physics, University of Vienna, Vienna, Austria;* <sup>4</sup>*Physical Sciences and Engineering Division, King Abdullah University of science and Technology, KAUST, Thuwal, Saudi Arabia*

Telechelic Star Polymers (TSPs) are macromolecules made of f diblock copolymers grafted on a central anchoring point. Each diblock arm has a fraction of a solvophobic (at the outside) and (1-a) solvophilic monomers. The dual nature of their arms makes TSPs particularly sensitive to

variations of the external conditions, such as temperature or ionic strength, which allows each particle to self-assemble into a soft particle with attractive patches on the surface. This gives rise to an unprecedented richness in the morphology of resulting material, which has been explored by computer simulations. The consequences on the dynamics have not been considered yet. Using a powerful combination of experiments and computer simulations with appropriately designed and synthesized TSPs (based of styrene-isoprene blocks with isoprene inside and different  $f$ , and molar mass), we demonstrate that these systems are simple, robust and tunable system. They can self-assemble hierarchically into soft-patchy particles and mechanically stabilized structures. By means of rheological investigations in the linear viscoelastic regime, we determine the liquid-to-solid transition upon cooling and discuss a surprising re-entrant liquid transition with continuing cooling. We find that, in general the mechanical properties of the gel is largely depending on the temperature (i.e., interparticle attraction strength) and the cooling rate. Moreover, the imposed shear reduces the elasticity of the gel by increasing the number of intra particle bonds. Finally, we examine the direct impact of inter-particle attraction strength on the yielding behavior of TSPs during start-up shear flow experiments.

## Symposium PM Polymer Melts: From Molecular Rheology to Processing

Organizers: Reza Foudazi and Richard Graham

Tuesday 9:50 Plaza I

PM1

### Microscopic theory of rheology and tube field instabilities of polymer liquids under continuous uniaxial extension

Kenneth Schweizer and Shijie Xie

*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We generalize our non-classical theory for the shear rheology of entangled chain polymer liquids (ACS MacroLetters, 7, 218 (2018)) to treat continuous startup uniaxial extension. The strain and deformation rate dependence of the entanglement grip force differs from that previously derived for shear. Transverse primitive path localization in a tube is functionally coupled to stress, polymer orientation and chain stretch. The tube confinement field is of finite strength, and thus can be weakened or destroyed (“tube instability”) under deformation. As a consequence, the engineering stress maximum is predicted to be observable only when the Rouse Weissenberg number  $WiR$  is less than a value of order unity. In a limited extension rate range bracketing  $WiR \sim 1$ , the overshoot Hencky strain scales as an apparent power law with an exponent of  $\sim 1/3$ . Globally, four distinct regimes of behavior are predicted. If  $WiR \ll 1$  (regime I), the tube field is always dynamically stable, implying homogeneous response including steady state flow. In contrast, for large  $WiR$  (regime IV) the engineering stress grows monotonically until tube confinement is destroyed at a Hencky strain that decreases with extension rate, and hence an overshoot does not exist in this regime. Between regimes I and IV a tube instability emerges after the engineering stress overshoot but in two distinct manners that are distinguished by the separation in strain between tube field destruction and the overshoot. In regime II this separation decreases with extension rate, while in regime III it increases. By identifying the microscopic tube confinement field instability with the onset of macroscopic non-uniform deformation, the theoretical four regime behavior is in good agreement with the phenomenology observed experimentally.

Tuesday 10:15 Plaza I

PM2

### Examining the nature of melt stretching of entangled melts

Zhichen Zhao and Shi-Qing Wang

*University of Akron, Akron, OH 44325, United States*

Large magnitude extension of crosslinked rubbers and noncrosslinked entangled melts is presumably rather well understood. For example, the chain deformation supposedly results in entropic forces that can be assigned to the effective entanglement strands. The recent investigation of ductile deformation of such melts below  $T_g$  [1] raises questions concerning the nature of intrachain forces that emerge during melt stretching. Can melt stretching, i.e., uniaxial extension of polymer melts above  $T_g$ , produce significant non-entropic forces? How to observe such forces? The present work aims to explore the answers to such questions.

[1] J. Chem. Phys. 141 (9), 094905 (2014).

Tuesday 10:40 Plaza I

PM3

### A coil-stretch transition in planar elongational flow of an entangled polymeric melt

Mohammad Hadi Nafar Sefiddashti, Brian J. Edwards, and Bamin Khomami

*Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, United States*

Virtual experimentation of atomistic entangled polyethylene melts undergoing planar elongational flow revealed an amazingly detailed depiction of individual macromolecular dynamics and the resulting effect on bistable configurational states. A clear coil-stretch transition was evident, in much the same form as first envisioned by de Gennes for dilute solutions of high polymers, resulting in an associated hysteresis in the configurational flow profile over the range of strain rates predicted by theory. Simulations conducted at steady state revealed bimodal distribution functions in which equilibrium configurational states were simultaneously populated by relatively coiled and stretched molecules, which could transition from one conformational mode to the other over a relatively long timescale at critical values of strain rate. The implication of such behavior points to a double-well conformational free energy potential with an activation barrier between the two configurational minima. The configurational hysteresis can also lead to a similar phenomenon with respect to the rheological properties of the fluid such as the extensional

viscosity. As a consequence, the experimental steady state viscosity could highly depend on the deformation history of the sample as will be discussed.

Tuesday 11:05 Plaza I

PM4

### **What is the microscopic origin of stress in entangled polymer melts?**

Wen-Sheng Xu, Christopher Lam, Jan-Michael Carrillo, Bobby Sumpter, and Yangyang Wang

*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

The classical theory of polymeric liquids attributes the stress to the orientation of the bond vectors of the polymer. For entangled polymers, both the phenomenological transient network models and the tube model adopt this hypothesis, reducing the problem of calculating stress to evaluating the conformation distribution of the “entanglement strands” or “tube segments”. Using molecular dynamics simulation, here we demonstrate that several basic premises of this classical theoretical treatment are in fact not fulfilled in the common coarse-grained bead-spring model of polymer melts, as well as a united-atom model of linear polyethylene. Specifically, we show that the segment distribution functions at the entanglement length scale and below exhibit considerable deviation from the theoretical predictions, in both the equilibrium and deformed states. Further conformational analysis reveals that the intrachain entropic stress at the entanglement length scale does not fully account for the total stress measured in the non-equilibrium molecular dynamics simulations of deformed polymer melts. These findings suggest that the aforementioned classical approximations may be inadequate for fully addressing the microscopic origin of stress in entangled polymer melts and are indicative of a considerable contribution from interchain entropy.

Tuesday 11:30 Plaza I

PM5

### **Unraveling dynamics of entangled polymers in strong extensional flows: An alternative to the tube model**

Soroush Moghadam<sup>1</sup> and Ronald G. Larson<sup>2</sup>

<sup>1</sup>*Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI, United States;* <sup>2</sup>*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States*

The traditional Doi-Edwards tube model, when applied to strong extensional flows at strain rates above the inverse Rouse time, predicts that the tube deforms affinely, which implies the extensional stress reaches its plateau as soon as the chain has become locally fully stretched, even if the chain is still folded, and far from being completely unraveled. By starting from a state in which the chain is in a locally fully stretched, but folded state, we develop an “entangled kink dynamics algorithm” that predicts the final unraveling of an ensemble of mutually entangled, folded chains, driven by a combination of drag forces and chain tension, with negligible Brownian motion. Equations for motions of both entangled folds and unentangled folds in which two chains hook together at a single fold point, are derived and solved, including the effects of constraint release that occurs when the end of one chain passes through the fold at which that chain is entangled. This model predicts that kinks move non-affinely, that the chain tension during unfolding is much less than predicted by the tube model, and that the stress approaches a plateau stress than in the tube model. The new model shows that in the folded state for fast extension, the entangled chains act like dilute ones.

## **Symposium AM Additive Manufacturing**

Organizers: Anthony Kotula and Patrick Anderson

Tuesday 9:50 Bellaire

*Keynote* AM14

### **Concentrated suspensions for 3D printing**

Didier Lootens

*Sika Technology, Zurich, Switzerland*

Additive manufacturing or 3D printing is already implemented in the fields of automotive, aeronautic, consumer products, medical, architecture, food and even construction where large scales are involved. Several material ranging from metals, plastic but also clay or concrete are used for additive manufacturing. The printing techniques are depending on the kind and form of materials used: (i) metal or plastic powders are selectively melts with a laser scanning a succession of 2D surfaces with the selective laser sintering (SLS) technique or bind with a curing agent extruded from a nozzle, (ii) thermoplastic in a form of pellets or filament are melts and extrude at high temperature to be deposited as a filament with the fused deposition modelling, (iii) photopolymers are solidified layer by layer with light source in the Stereolithography technique or injected onto a build tray and cured using UV light. Each technique has its advantages and drawback such as energy consumption (laser, high temperature), materials performances and recycling (powder), high material cost and relatively slow processes. Additive manufacturing allows high complexity but at a lower resolution than subtractive manufacturing requiring in some applications a post treatment of the surfaces to obtain the same quality (hybrid manufacturing). Among alternative 3D printing technology, the Direct Ink Printing demonstrates huge advantages. In this technique, concentrated suspensions are pumped and deposited layer by layers in similar way than FDM, but the solidification occurs with physico-chemical reactions. The technique is 1000 times faster than FDM and reach similar resolution than SLS with a hybrid treatment. The design of the concentrated suspensions used are representing huge challenges as the material should follow contradictory requirements: (i) it should be pumped from a reservoir to the printing head and then extruded through a nozzle, be fluid enough but not demonstrate segregation, neither flow under gravity, (ii) ones deposited, the material should not flow under its own weight, (iii) a given layer should be able to support subsequent upper layers. The control of the interactions between the particles in a concentrated suspension is then primordial. Not only the control of the yield stress and

the thixotropy are mandatory but also the understanding and control of the jamming is required to reduce the liquid part and reach high performance materials. We demonstrate how the understanding and control of the rheology is central to introduce a new disruptive transition of cost and speed in the additive manufacturing industry.

Tuesday 10:15 Bellaire

AM15

### **Structure-mechanical property relationship in UV-cured acrylate systems**

Rosaria Anastasio, Ruth Cardinaels, Gerrit Peters, and Lambert van Breemen

*Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands*

Stereolithography is an additive manufacturing process in which the products are built layer-by-layer from a UV-curable material. Typically, the mechanical properties of the 3D-printed product are affected by the intrinsic material heterogeneity along the sample thickness. To understand what determines this heterogeneity, single layers of UV-curable polymer are characterized. To that end, micrometer-sized pillars and dog-bone shaped samples have been prepared via UV-curing. First, mixtures of pure bisphenol-A ethoxylate diacrylate, BisDAn=2, monomer were characterized and the evolution with irradiation time of conversion and glass-transition temperature,  $T_g$ , was studied. Subsequently, micro-compression measurements on maximally cured micropillars were performed to study possible size effects [1]. The results show a reduction in yield stress for decreasing pillar size. Moreover, tensile measurements were performed on dog-bone shaped samples and the results show higher yield stress values, when compared with compression tests. This effect can be attributed to the rinsing with acetone during the sample preparation, which was verified by means of NMR and GPC characterization of the rinsing liquid. Next, the effect of the molecular mobility and the resin formulation on the conversion and ultimate mechanical properties has been studied. Three mixtures of BisDAn=2 with different amounts of tetraethylene glycol diacrylate (TEGDA) (0, 10, 30 wt%) were characterized. FTIR tests show that enhanced conversion is achieved by adding a higher amount of TEGDA. This gives rise to an increase in  $T_g$  and strain hardening of cured samples. The correlations between, on the one hand, resin formulation and process conditions and, on the other hand, the final mechanical properties of UV-cured systems are established allowing to optimize the structure-mechanical properties relationship in acrylate networks.

[1] Guruprasad, T. S.; Bhattacharya, S.; S. Basu; *Polymer* 2016, 98:118 - 128.

Tuesday 10:40 Bellaire

AM16

### **Direct write of UV curable polymer-bonded magnets**

Alan Shen<sup>1</sup>, Anson Ma<sup>1</sup>, Sameh Dardona<sup>2</sup>, and Callum Bailey<sup>2</sup>

<sup>1</sup>*Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06268, United States;* <sup>2</sup>*United Technologies Research Center, East Hartford, CT 06108, United States*

Today, almost all commercial magnet manufacturers are using the conventional production method based on magnetic powder compaction and sintering. Alternatively, magnetic powder may be embedded directly within a polymer to produce “polymer-bonded magnets”. The latter method has recently gained popularity because of the design freedom in terms of complex shapes. Compared to the conventional sintering process, the maximum energy product  $(BH)_{max}$  of polymer-bonded magnets is generally lower. However, the fabrication of polymer-bonded magnets does not require high temperature sintering, reducing the associated costs and processing time. A new additive manufacturing method coined “UV-assisted direct write” (UVADW) has been developed to produce polymer-bonded magnets at room temperature. The UVADW method involves mixing magnetic powder (Nd-Fe-B) with a photo-curable binder to create an ink, which is then extruded through a nozzle and deposited onto a substrate. Understanding the ink rheology is critical to ensuring the printability and the shape fidelity of the printed structures. Parameters explored include the shape and polydispersity of the Nd-Fe-B particles with the ultimate goal to maximize the loading of the magnetic particles and consequently the magnetic performance.

Tuesday 11:05 Bellaire

AM17

### **Multimaterial 3D printing of silica-titania glass: Predictive tuning of suspension rheology**

Nikola Dudukovic<sup>1</sup>, Lana Wong<sup>1</sup>, Du Nguyen<sup>1</sup>, Joel Destino<sup>2</sup>, Timothy Yee<sup>1</sup>, Frederick Ryerson<sup>1</sup>, Tayyab Suratwala<sup>1</sup>, Eric Duoss<sup>1</sup>, and Rebecca Dylla-Spears<sup>1</sup>

<sup>1</sup>*Lawrence Livermore National Laboratory, Livermore, CA, United States;* <sup>2</sup>*Creighton University, Omaha, NE, United States*

The ability to 3D print transparent glass could impact applications ranging from microfluidics to optics. Multimaterial printing offers incorporating diverse functionalities by spatial control of material composition. The addition of dopants such as titania to silica glass can impart modifications in the optical or mechanical properties of the material. In this regard, multimaterial additive manufacturing (AM) of glass could enable advanced optics with tailored properties. However, a lack of predictive methodology is frequently a bottleneck in material development for AM. Hence, exploration of new printable materials often relies on trial and error, which is time-consuming, labor-intensive, and costly. We overcome these issues by quantifying and controlling the rheology of colloidal suspensions for direct ink writing (DIW) of silica-titania glass. We formulate inks from suspensions of fumed silica in an organic solvent with a dissolved molecular titania precursor. The multimaterial construct is printed from two inks (doped and undoped), then heat treated to form a dense, transparent glass. Since this process is extremely sensitive to ink formulation and discrepancies in solids loading, it is challenging to control the printability and compatibility of these inks. We use a small set of experimental data and estimates of interaction potentials to develop a predictive tool that allows us to design and obtain compatible inks without additional chemical species. Using this approach, we can formulate inks that are well-matched both in desired rheological properties as well as total solids

loading. We validate the model predictions and find that the rheology can be tuned for given process parameters. We print a multimaterial object from these inks to produce a transparent glass with spatial change in refractive index.

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## Symposium PS Polymers in Solution

Organizers: Nicolas J. Alvarez and Cari Dutcher

Tuesday 9:50 Post Oak

PS14

### **Impact of molecular weight distribution in developing crystalline morphology of gel-spun UHMWPE fibers**

Christopher K. Henry, Giuseppe R. Palmese, and Nicolas J. Alvarez

*Chemical Engineering, Drexel University, Philadelphia, PA 19104, United States*

Ultra-high molecular weight polyethylene (UHMWPE) fibers have been extensively studied because of their remarkable tensile modulus and strength. Most researchers agree these properties are due in part to the development of extended chain crystalline domains, commonly known as shish. Recent work has focused on models for the development of this structure during post-drawing but has assumed that starting structure is constant or irrelevant to the ultimate final properties. In our previous study we showed how the initial crystalline structure is strongly dependent on the extensional strain rate applied during gel-spinning, and that this structure evolves in a unique manner in the initial stages of post-drawing. We have continued this work by investigating how the precise molecular weight distribution of the UHMWPE used in spinning also affects the morphology of the spun fibers. Fibers are spun using an apparatus designed and built to allow for precise control of the spinning process. Extensional strain rate applied to the fibers is observed and correlated to the resultant structure as measured through the use of small angle and wide angle x-ray scattering.

Tuesday 10:15 Post Oak

PS15

### **Dripping-onto-substrate (DoS) extensional rheometry of low-viscosity printing inks: Effect of varying concentration and molecular weight of the polymer binders**

Samrat Sur, Maxime Rosello, and Jonathan Rothstein

*Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, MA, United States*

The influence of polymers concentration on the drop formation and filament breakup has been widely studied both experimentally and numerically for monodisperse polymer solutions in the dilute regime up to the coil overlap concentration  $c^*$ . In this study, we will show how the addition of a highly polydisperse binder to a low viscosity solution in the semi dilute regime can have a dramatic influence on the drop formation and filament thinning dynamics. For low shear viscosity polymer solutions, the jet breakup is initially governed by a balance of inertial and capillary stresses. Whereas, for a viscous polymer solution, the thinning dynamics is initially governed by the balance between the viscous stresses and capillary stresses before transitioning to a balance of viscoelastic and capillary stresses at later times. This transition occurs at a critical time when the radius decay dynamics shift from a  $2/3$  power law or linear dependence to an exponential decay as the increasing deformation rate imposed on the fluid filament results in large molecular deformations and rapid crossover into the elastocapillary regime. In this study, we will compare four different binders with different polymer architectures and show its effect on the capillary breakup thinning dynamics of polymer solutions generally used in coating and printing industry. Using the Dripping onto Substrate (DoS) Extensional Rheometry, the dynamics of drop break-up and pinch off will be presented for a series of binders of varying molecular weight and concentration. Molecular weights of the binders varied between 50kg/mol to 200kg/mol and the concentrations varied between  $2c^*$  to  $5c^*$ . We will also show a significant difference in the filament breakup of binders of similar molecular weight and solution viscosity by characterizing the thinning dynamics into different regimes. Finally, the extensional rheology will be directly correlated to the result of jet breakup studies for these low-viscosity idealized printing inks.

Tuesday 10:40 Post Oak

PS16

### **Stretched polymer physics, pinch-off dynamics and printability of polymer solutions**

Jelena Dinic<sup>1</sup>, Madeleine Biagioli<sup>2</sup>, and Vivek Sharma<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Univ of Illinois - Chicago, Chicago, IL 60607, United States;* <sup>2</sup>*Chemical Engineering, Univ of Illinois - Chicago, Chicago, IL 60630, United States*

Free surface flows and drop formation processes present in printing, jetting, spraying, and coating involve the development of columnar necks that undergo spontaneous surface-tension driven instability, thinning, and pinch-off. Stream-wise velocity gradients that arise within the thinning neck create an extensional flow field, which induces micro-structural changes within complex fluids that contribute elastic stresses, changing the thinning and pinch-off dynamics. We show that visualization and analysis of capillary-driven thinning and pinch-off dynamics of the columnar neck in an asymmetric liquid bridge created by dripping-onto-substrate can be used for characterizing the extensional rheology of complex fluids. Using a particular example of dilute and semi-dilute aqueous PEO solutions, we show the measurement of both the extensional relaxation time and extensional viscosity of weakly elastic, polymeric complex fluids with low shear viscosity ( $< 20$  mPa.s) and relatively short relaxation time ( $< 1$  ms). Characterization of elastic effects and extensional relaxation times in these dilute and many semi-dilute solutions is beyond the range measurable in the standard geometries used in commercially available shear and extensional rheometers (including CaBER, capillary breakup



extensional rheometer). Furthermore, we use dripping-onto-substrate (DoS) extensional rheometry technique for examining the influence of extensibility, flexibility and concentration on pinch-off dynamics and extensional rheology response of aqueous polyethylene oxide (PEO) solutions and aqueous 2-Hydroxyethyl cellulose (HEC) solutions. We show that the magnitude and concentration-dependence displayed by extensional viscosity and extensional relaxation time are quite distinct from the values obtained in response to shear flow, as the progressive screening of excluded volume and hydrodynamic interactions depends on polymer concentration as well as on degree of stretching and conformational anisotropy.

Tuesday 11:05 Post Oak

PS17

### **Effect of fluid contact angle on filament thinning and break-up of high surface tension polymer solutions in extension**

Ravi Neelakantan, Jerome Unidad, Elif Karatay, Eric Cocker, Palghat Ramesh, and David Johnson  
*Hardware Systems Laboratory, PARC, A Xerox Company, Palo Alto, CA 94304, United States*

The Filament Extension Atomizer™ (FEA) is a novel technology for creating aerosols and mists of highly viscous and strain hardening fluids. A thin film of fluid is processed between two diverging surfaces, which creates thin filaments that quickly succumb to surface tension and break into narrowly dispersed droplets. While we have observed the importance of surface wetting of the two surfaces experimentally during atomization, particularly for high surface tension fluids, the fundamental physics are not well understood. To study the effects of end-plate wetting a custom-built Capillary Break-up Extensional Rheometer (CABER) with interchangeable end-plate materials was studied with a high surface tension polymer solution. The end-plate materials varied from highly wetting to non-wetting and were combined in various symmetric and asymmetric orientations to comprehensively investigate the effects. Filament formation, thinning, and break-up, as well as apparent relaxation time and fluid migration were dramatically affected by both wetting and symmetry at a fluid sample size. The onset of filament formation spanned over an order of magnitude depending on the wetting behavior and symmetry of the end-plates. The highly asymmetric scenarios displayed the most striking differences from classic CABER experiments. Through manipulation of the wetting behavior at the ends, filament break-up times can be changed by an order of magnitude and fluid migration can vary by five-fold.

Tuesday 11:30 Post Oak

PS18

### **Extensional flow behavior of methylcellulose solutions containing fibrils**

Svetlana Morozova<sup>1</sup>, Peter W. Schmidt<sup>2</sup>, Athena E. Metaxas<sup>2</sup>, Frank S. Bates<sup>2</sup>, Timothy P. Lodge<sup>2</sup>, and Cari S. Dutcher<sup>3</sup>

<sup>1</sup>*Department of Chemistry, University of Minnesota, Minneapolis, MN, United States;* <sup>2</sup>*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, United States;* <sup>3</sup>*Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States*

Methylcellulose (MC), a methoxy-substituted cellulose ether, is used in a variety of food, pharmaceutical, construction, and consumer applications due to its solubility in water at low temperatures. In addition to its solubility at low temperatures, MC reversibly transitions to a turbid hydrogel upon heating or upon the addition of NaCl to the solution. The gelation phenomenon in aqueous MC solutions is due to the formation of a fibrillar network. While the small amplitude oscillatory and large amplitude oscillatory shear rheological behavior has been characterized for MC solutions, the extensional flow behavior has not been reported. Capillary breakup extensional rheometry (CaBER) was used to characterize aqueous MC solutions with 8 wt% NaCl and aqueous solutions without salt at room temperature. Without NaCl, the solutions only exhibit power law behavior whereas solutions with NaCl exhibit both power law and elastic deformation profiles. As MC concentration increases, both the extensional relaxation time and the apparent extensional viscosity increase. This behavior is attributed to the presence of fibrils in the MC solutions containing NaCl annealed at room temperature. The study of the extensional behavior of this already commercially relevant polymer enables new ways to process MC, such as fiber spinning and extrusion. Finally, ongoing work using microfluidic filament stretching will be presented for determining the extensional viscosity for MC systems.

## **Symposium DA Design of Applied Materials**

Organizers: Jeffrey Martin and Matthew J. Armstrong

Tuesday 9:50 San Felipe Room

DA1

### **Viscosities in coatings industry: Shear vs. extension**

Yu Wang<sup>1</sup> and Hao Sun<sup>2</sup>

<sup>1</sup>*PPG, Pittsburgh, PA, United States;* <sup>2</sup>*Rheology Control Platform, PPG Industries, Inc., Allison Park, PA 15101, United States*

It is well known that the extensional rheology of paints is highly correlated with their application performance, due to the elongational flows they are subjected to during processes such as spray or roller application. However, due to instrumental limitations, the measurement of extensional rheology has yet to be widely applied in the coatings industry. In this talk, we will discuss a few cases where extensional rheology provides us insight which is not available through conventional shear rheology measurements.

Tuesday 10:15 San Felipe Room

DA2

**Characterizing and designing printability, spinnability, jettability, sprayability or stickiness of complex fluids and soft materials**Vivek Sharma, Jelena Dinic, Leidy N. Jimenez, and Carina Martinez*Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

Designing soft materials with appropriate processability characteristics, often expressed in heuristic terms such as sprayability, spinnability, stickiness and printability, requires a systematic control over their response to both shear and extensional deformations. Liquid transfer and drop formation/deposition processes involve complex free-surface flows including the formation of columnar necks that undergo spontaneous capillary-driven instability, thinning and pinch-off. For simple (Newtonian and inelastic) fluids, a complex interplay of capillary, inertial and viscous stresses determines the nonlinear dynamics underlying finite-time singularity as well as self-similar capillary thinning and pinch-off dynamics. In rheologically complex fluids, extra elastic stresses as well as non-Newtonian shear and extensional viscosities dramatically alter the nonlinear dynamics. Stream-wise velocity gradients that arise within the thinning columnar neck create an extensional flow field, and many complex fluids exhibit a much larger resistance to elongational flows than Newtonian fluids with similar shear viscosity. Characterization of pinch-off dynamics and the response to extensional flows requires bespoke instrumentation not available, or easily replicated, in most laboratories. Here we show that dripping-onto-substrate (DoS) rheometry protocols that involve visualization and analysis of capillary-driven thinning and pinch-off dynamics of a columnar neck formed between a nozzle and a sessile drop can be used for measuring shear viscosity, power law index, extensional viscosity, relaxation time and the most relevant processing timescale for printing or spraying. We elucidate the critical influence of polymer concentration, flexibility, charge, hydrophobicity and extensibility determine on capillary-driven thinning and pinch-off dynamics, extensional rheology and consequently on spinnability and printability of a wide range of polymeric complex fluids.

Tuesday 10:40 San Felipe Room

DA3

**Inverse problems in linear viscoelastic material design**R. E. Corman<sup>1</sup>, Jan Vermant<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup><sup>1</sup>*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Department of Materials, ETH Zürich, Zürich, Switzerland*

We explore blueprints for designing microstructures to achieve arbitrary shapes of linear viscoelastic relaxation spectra, including emulsions, colloidal dispersions, polymer solutions, and polymer melts. Optimal viscoelastic spectra arise in a range of applications including vibration absorption, adhesion, automotive systems, biomedical devices, and soft robotics. The targeted spectra might be achieved by several different material microstructures which frames an inverse problem in design of rheologically-complex materials. In principle, materials can be designed to achieve relaxation times covering an incredibly wide range. However, designing the specific shape of an arbitrary spectrum, across a wide range of timescales, moduli, and viscosity, is non-trivial. We study multiple material paths, with detailed blueprints, to achieve targeted relaxation behavior. Examples include a power-law spectrum typically associated with critical gels but achieved with non-interacting dilute suspensions of emulsion droplets, Brownian hard spheres, or Brownian hard spheroids. Other more complex targets and formulations are also considered. Manufacturability constraints and inherent spectral shapes of components (e.g. Rouse, Zimm) restrict design freedom for arbitrary viscoelastic design. We discuss such engineering limitations and possible counter measures. Our previous work[1-3] described methods for identifying material-agnostic targets for viscoelasticity through design optimization techniques. The work here begins to close the loop in this top-down design process for rationally incorporating rheologically-complex materials to improve engineering design.

[1] Corman, R. E., Rao, L., Ashwin Bharadwaj, N., Allison, J. T. & Ewoldt, R. H., *J. Mech. Des.* 138, 51402 (2016); [2] Lee, Y. H., Corman, R. E., Ewoldt, R. H. & Allison, J. T., *Des. Autom. Conf.* 1-12 (2017).; [3] Corman, R. E., Lee, Y. H., Allison, J. T. & Ewoldt, R. H., *Annual Meeting of the Society of Rheology* (2017).

Tuesday 11:05 San Felipe Room

DA4

**Field-sensitivity of flow predictions to rheological parameters**Jonathan B. Freund, Jaekwang Kim, and Randy H. Ewoldt*University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We ask this question: where in a flow is a quantity of interest  $Q$  quantitatively sensitive to the model parameters  $\theta$  describing the rheology of the fluid? This field sensitivity is computed via the numerical solution of the adjoint flow equations, as developed to expose the target sensitivity  $\delta Q/\delta\theta(x)$  via the constraint of satisfying the flow equations [1]. Our primary example is a sphere settling in Carbopol, for which we have experimental data, though we also study a four-parameter Moore model for a generic thixotropic fluid. For this model configuration, we simultaneously calculate how much a *local* change in the rheological model parameters affect the resistance. Such field sensitivities can show where different fluid physics in the model (time scales, elastic versus viscous components, *etc.* are important for the target observable and generally guide model refinement by prioritizing behaviors important for the predictive goals. In this case, the computational cost of solving the local sensitivity problem is negligible relative to the nonlinear flow problem. The sphere example is illustrative; the true utility of field sensitivity is in the design and analysis of less intuitive flows, for which we provide some additional examples.

[1] Freund JB, Kim J & Ewoldt RH (2018) Field sensitivity of flow predictions to rheological parameters. *J Nonnewton Fluid Mech* **257**:71-82. doi: 10.1016/j.jnnfm.2018.03.013

Tuesday 11:30 San Felipe Room

DA5

**Deciphering the adhesive properties of mussel-inspired metal-coordinate physical gels**Erica Lai<sup>1</sup>, Bavand Keshavarz<sup>2</sup>, and Niels Holten-Andersen<sup>1</sup><sup>1</sup>*Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;* <sup>2</sup>*Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

In recent years, researchers have incorporated mussel-inspired metal coordination into various types of gels to improve their mechanical properties, particularly toughness and self-healing. However, not much is understood about how known methods for tuning the viscoelastic spectrum of these gels affect their adhesive properties. In this study, both rheological and tack tests are performed on metal-coordinate physical gels comprised of 4-arm polyethylene glycol end-functionalized with histidine (His) and divalent metal ions ( $M^{2+}$ ). Understanding how the ligands participate in each of the  $His_nM^{2+}$  species within a gel helps us determine the correlations between linear mechanical properties (i.e. plateau modulus, characteristic relaxation time) and resulting non-linear behavior (i.e. peak stress, adhesion energy). With this understanding, incorporating metal coordination into adhesive materials could provide condition-dependent control of adhesive properties.

## Symposium BA Biological and Active Matters

Organizers: Pushkar Lele and Kelly Schulz

Tuesday 9:50 Tanglewood

BA14

**Transient modeling of viscoelasticity, thixotropy, and flow inhomogeneities (syneresis) in human blood rheology**Jeffrey S. Horner, Antony N. Beris, and Norman J. Wagner*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Blood is a complex fluid primarily composed of deformable red blood cells (RBCs) suspended in an aqueous plasma. As a result of aggregates of RBCs, termed rouleaux, that form at rest and under low shear, blood exhibits interesting rheological signatures including a shear thinning behavior, viscoelasticity, and thixotropy. At low shear conditions, a phenomenon known as syneresis can also occur, in which a RBC depletion layer forms near the walls of the measurement device due, in part, to the relatively large aggregate size and the significant difference between the plasma and bulk viscosities. Understanding the complex rheology of blood is critical both for developing blood flow simulations throughout the circulatory system and for engineering rheological diagnostics tools for diseases that have been shown to affect the rheology of blood. In this work, we present new data on step shear change and cessation measurements for healthy human blood using an improved measurement protocol developed in our laboratory [1]. Using these data, we propose a two fluid model, which is incorporated into a previously developed model for transient blood rheology [2], to capture the effects of syneresis. This analysis helped to better identify the complex viscoelastic behavior associated with rouleaux. The structure-dependent viscoelasticity is characterized through a viscoelastic network approach. The new model is compared to the new measurements and demonstrates a good fit to the experimental data. Additionally, the new model improves upon the previous model predictions for unidirectional large amplitude oscillatory shear, demonstrating the full capability of the new model. This work helps to elucidate the connection between the bulk flow properties of blood and the underlying microstructure, and further, introduces transient modeling concepts that can be applied to a broader range of viscoelastic and thixotropic fluids.

[1] Horner et al., Clin. Hemorheol. Microcirc., Preprint, (2018). [2] Horner et al., J. Rheol., 62(2), (2018).

Tuesday 10:15 Tanglewood

BA15

**Contemporary modeling and analysis of human blood rheology with recently developed models, experimental and analysis techniques**Matthew J. Armstrong<sup>1</sup>, Norman J. Wagner<sup>2</sup>, Antony N. Beris<sup>2</sup>, Jeffrey S. Horner<sup>2</sup>, Timothy Hill<sup>1</sup>, and Charles Keith<sup>3</sup><sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States;* <sup>3</sup>*United States Military Academy, Westpoint, NY, United States*

Recent work modeling the rheological behavior of blood indicates that blood has all of the hallmark features of a complex material, including shear-thinning, viscoelastic behavior, a yield stress and thixotropy. After decades of modeling steady state blood data, and the development of steady state models, like the Casson, Herschel-Bulkley, etc. the advancement and evolution of blood modeling to transient flow conditions now has a renewed interest. Using recently collected human blood rheological data we show and compare modeling efforts with several new models including the Horner-Armstrong-Wagner-Beris (HAWB), the VE-MDTM, and more. We will compare the new approaches, along with discussion of how we have integrated thixotropic and viscoelastic features for each new model. This is followed with a discussion of novel transient flow rheological experiments applied to human blood including for model fitting purposes including step-up/step-down, sawtooth experiments and Large Amplitude Oscillatory Shear (LAOS) flow. The family of models that can handle these transient flows involve modifications to the recently published Modified Delaware Thixotropic Model (MDTM), the HAWB and the Bautista-Monero-Puig Model (BMP). Lastly we demonstrate a novel approach to analyzing transient blood data by incorporating the novel Series of Physical Phenomena (SPP) framework, and proposed SPP-Lambda. Recent work with blood using LAOS and transient data has shown that its unique rheological signature can be used as a pseudo-“fingerprint”, able to clearly show and delineate elastic and viscous regions of the LAOS cycle. Applying large amplitude oscillatory shear (LAOS)

to complex fluids induces nonlinear rheological responses, that, with proper LAOS analysis technique, can be used to sensitively probe the underlying microstructure and its dynamics. This is done with our recently acquired blood data.

Tuesday 10:40 Tanglewood

BA16

### **Swimming to stability: Activity-doped colloidal gels**

Ahmad K. Omar, Yanze Wu, Zhen-Gang Wang, and John F. Brady

*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

External fields can entirely alter the free energy landscape of soft materials and can be exploited as a powerful tool for the assembly of targeted nanostructures. Here, we use computer simulations to demonstrate that internal fields -- nonequilibrium forces that are internally generated in the system -- in the form of active particles can precisely modulate the dynamical and energetic landscape of a model soft material, a colloidal gel. Embedding a small fraction of active particles within a gel can provide a unique pathway for the dynamically frustrated network to circumvent the kinetic barriers associated with reaching a lower free energy state via thermal fluctuations alone. Moreover, by carefully tuning the active particle properties (the propulsive swim force and persistence length) in comparison to the appropriate micromechanical properties of the gel, active-mediated depletion-like forces can emerge -- despite no geometric size asymmetry between gel and active particles -- and push the system towards disparate regions of phase space. Interestingly, the boundaries of our dynamic phase diagram can be altered by simply tuning the solvent viscosity. Our findings highlight the potential wide-ranging structural control facilitated by varying the dynamical properties of a remarkably small fraction of driven particles embedded in a host material.

Tuesday 11:05 Tanglewood

BA17

### **Continuum modeling of nanoparticles transport in vivo through bifurcations**

Rekha R. Rao<sup>1</sup>, Jonathan Clausen<sup>1</sup>, Dan S. Bolinteanu<sup>1</sup>, Justin Wagner<sup>2</sup>, Kim Butler<sup>3</sup>, Richard Martin<sup>4</sup>, Zixiang Liu<sup>5</sup>, and Cyrus Aidun<sup>5</sup>

<sup>1</sup>*Fluid and Reactive Processes, Sandia National Laboratories, Albuquerque, NM 87185-0836, United States;* <sup>2</sup>*Aerosciences Department, Sandia National Laboratories, Albuquerque, NM 87180-0825, United States;* <sup>3</sup>*Nanobiology, Sandia National Laboratories, Albuquerque, NM 87108, United States;* <sup>4</sup>*Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87131, United States;* <sup>5</sup>*The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

We are developing a multiscale modeling approach to support targeted drug delivery of nanomedicines and better understand nanoparticle (NP) transport in vivo. In this presentation, we will discuss our work to develop a model of NP transport in the blood vessels with bifurcations. We compare two types of rheological models for the blood: one using a Casson model with a yield stress and another where we track the concentration of red blood cells explicitly and use this for the generalized Newtonian viscosity model. The continuum model for transport of the NPs is coupled to the rheology of the blood through the velocity field and a diffusivity tensor. The NP diffusion tensor is informed through experiment, literature review, and particle-scale modeling of the red blood cell-NP interactions. The particle-scale modeling has shown that the diffusivity tensor is anisotropic, and behaves differently in the shear, vorticity and flow directions. The off-diagonal terms are small implying that a flow aligned tensor representation of the diffusivity may work well. We compare this approach to the standard method using an isotropic diffusivity tensor for dilute small particles in a continuous fluid. Micro-particle imaging velocimetry from high speed videos of confocal microscopy of fluorescent NP in the large bifurcated vessel in the vasculature of a chicken embryo model (CAM) system is discussed. The predictions for blood flow and particle transport are compared to imaging data with a bifurcation. This imaging was also used to create the mesh for the numerical methods, giving the data and the model a consistent geometry.

\* Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Tuesday 11:30 Tanglewood

BA18

### **Mechanical shape programming of double network liquid crystal elastomers**

Morgan G. Barnes<sup>1</sup> and Rafael Verduzco<sup>2</sup>

<sup>1</sup>*Materials Science and NanoEngineering, Rice University, Houston, TX 77005, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Liquid crystal elastomers (LCEs) are shape-responsive materials that combine the elasticity of rubbery polymer networks with the responsiveness of liquid crystals. Shape changes in LCEs are coupled to changes in the liquid crystal order parameter but typically limited to simple deformations such as uniaxial extension or contraction. Recent work has demonstrated that patterning of the liquid crystal director in LCE films can give rise to a variety of non-planar deformations, but these approaches are limited to thin films and two-dimensional patterning of the liquid crystal director. Here, we show that through optimization of network chemistry along with mechanical shape programming, a range of fully reversible three-dimensional shape changes can be achieved in bulk LCEs. Double network LCEs are synthesized through a thiol Michael addition reaction to define the first network followed by radical photopolymerization of residual acrylate functional groups to produce a second interpenetrating network. The resulting LCEs reversibly transition between shapes defined by the first and second network crosslinking reactions, and the shape responsiveness can be optimized by tailoring the crosslink density and moduli of the first and second networks. We quantify the roles of strain, network crosslink density, network composition, and sample thickness on the fidelity of the resulting imprinted shapes. Using optimized network

compositions, we demonstrate the ability to engrave patterns and program non-planar shape changes in LCEs including LCE sheets that reversibly curls into a flower and a flat LCE sheet that reversibly transitions to a topographical map of a face. Our work elucidates the role of network structure on shape-responsiveness in LCEs and demonstrates a general approach to produce complex and reversible shape-responsive materials.

## Symposium NF Non-Newtonian Fluid Mechanics & Flow Instabilities

Organizers: Aditya Khair and Christian Clasen

Tuesday 9:50 Plaza II

NF1

### **Wormlike micelle instabilities: Rheology fundamentals**

Laetitia Pinaud, Pascal Herve, and Guillaume Ovarlez

*Laboratoire du Futur, Pessac, France*

Polymer solutions have many applications in industry. Their main issue is the irreversible breakage of the polymer chains under high shear rate. An alternative to avoid it is to use giant micelles, also called wormlike micelles (WLM). WLM solutions have a rheological behavior similarly to polymer solutions. The surfactants used in this study are long chain Alkyl amidopropyl betaines. At a fixed volume fraction and under controlled conditions, the viscosity increases and decreases with temperature in varying temperature ranges depending on shear rate. A possible reason for this behavior could come from elastic instabilities. Many studies have been done on WLM instabilities. Most of them dealt with the occurrence of shear banding within the shear stress plateau. Our system despite having such a plateau does not display shear banding (thanks to the optic visualization of S. Lerouge) In this work, we study the fundamentals of this fluid which are not as simple as one might expect. We first perform experiments of constant stress step. Laminar flows are then obtained only when a low stress value ( $< 1\text{Pa}$ ) is imposed, corresponding to the instability threshold. In these conditions, long transient states are observed and steady state is obtained after a long time (500s). The related shear rates are very low ( $< 10^{-4}\text{ s}^{-1}$ ), explaining why laminar flows are difficult to obtain with such materials. We propose a viscoelastic model to describe these observations: it is characterized by a long relaxation time, a very high viscosity and a low elastic modulus which is consistent with the stress plateau and the onset of elastic instabilities. We also performed constant shear rate experiments. When the shear rate is lower than the critical shear rate, the viscoelastic fluid behavior is recovered. When it is higher than the critical shear rate, a stress overshoot is observed and the instability is triggered. The height of this overshoot varies with the resting time: the maximum stress can be higher up to 20 times the steady state value

Tuesday 10:15 Plaza II

NF2

### **Effect of varying fluid rheology on viscoelastic fluid-structure interactions between a flexible cylinder and wormlike micelle solution**

Anita Dey, Yahya Modarres-Sadeghi, and Jonathan Rothstein

*Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

For a cylinder in Newtonian fluid flow, alternating shedding vortices at high Reynolds numbers can drive the motion of the structure resulting in Vortex-Induced Vibration (VIV). Unlike Newtonian fluids, the flow of viscoelastic fluids can become unstable even at infinitesimal Reynolds numbers due to a purely elastic flow instability occurring at large Weissenberg numbers. We have recently shown that elastic flow instabilities can drive the motion of a number of different flexible structures including sheets and cylinders. The fluctuating fluid forces exerted on the structure from the elastic flow instabilities can grow large enough to result in significant motion of the flexible structure. This motion of the flexible cylinder has been characterized into periodic 1D and 2D oscillations. In this talk, we will present an investigation into the effects of varying fluid viscosity and relaxation time on the oscillatory response of the flexible structure. These effects will be discussed in terms of the elastic Mach number in order to distinguish the complex flow instabilities observed during the 1D and 2D flexible cylinder oscillations. The occurrence of the oscillations of a flexibly mounted, rigid cylinder at a frequency comparable to the structural natural frequency will be studied to further investigate the possibility of a window of lock-in behavior for viscoelastic fluid-structure interactions. The static and dynamic responses of the flexible cylinder will be presented for a range of flow velocities and varying fluid rheologies, along with measurements of velocity profiles and flow-induced birefringence, in order to quantify the time variation of the flow field and the state of stress in the fluid.

Tuesday 10:40 Plaza II

NF3

### **Sphere sedimentation in wormlike micelles: The role of relaxation spectrum and extensional gradients**

Shijian Wu and Hadi Mohammadigoushki

*Chemical and Biomedical Engineering, Florida State University, Tallahassee, FL 32310, United States*

Beyond a critical extensional Deborah number, a falling sphere in wormlike micelles never reaches a constant terminal velocity as in many other solutions, it settles with an unsteady velocity instead. Recent studies have shown that the chain scission of wormlike micellar at the wake of a sphere might lead to this behavior. Similar instabilities are also observed in viscoelastic polymer solutions where chain scission is unlikely happen. The reasons of instabilities in polymer solutions are thought to be the results of a single-mode relaxation spectrum of the polymer chains or the asymmetry of the polymer chain extensions at the side of the falling sphere. The effects of micellar relaxation spectrum and gradients in micellar extensions over a wide range of elasticity ( $10^{-2} < De_E < 15$ ) and inertia ( $10^{-6} < Re < 10$ ) are tested in this project. Falling spheres exhibit fluctuating behavior in wormlike micelles with a single-mode relaxation spectrum for  $De_E \leq 2.6$ . However, spheres never exhibit the unsteady motion in the

wormlike micelles with a broad relaxation spectrum (i.e. a multi-mode Maxwell model). The results show the importance of the micellar relaxation spectrum on dynamics of the sphere sedimentation in wormlike micelles. We show that a criterion based on the ratio of dissipated energy to the stored elastic energy of micelles can successfully describe the effect of micellar relaxation spectrum on sphere sedimentation dynamics.

Tuesday 11:05 Plaza II

NF4

### **Effect of confinement on velocity profiles in pressure driven flow of wormlike micelle solutions**

Paul F. Salipante and Steven Hudson

*Polymers and Complex Fluids Group, National Institute of Standards and Technology, Gaithersburg, MD 20910, United States*

We investigate the effect of confinement on the velocity profiles of shear banding wormlike micelle solutions in pressure driven capillary flow. Velocity profiles are obtained using holographic 3d particle tracking velocimetry on the fluids seeded with microparticles. The velocity profiles measured at different volumetric flow rates are compared to expected velocity profiles determined from rotational rheometry. Capillary rheology measurements are performed simultaneously via measurements of flow rate and pressure drop across the capillary. While capillary rheology measurements yield viscosity values consistent with rotational rheometry, we observe deviation between the measured and expected velocity profiles that becomes more significant as the flow rate increases. We attribute the deviation to the finite interfacial width between the two shear bands. We compare our flow profile results to theoretical models that include nonlocal terms to describe the interfacial contribution to the total stress.

Tuesday 11:30 Plaza II

NF5

### **Transient evolution of shear bands in a model wormlike micellar solutions**

Alireza Dalili<sup>1</sup> and Hadi Mohammadigoushki<sup>2</sup>

<sup>1</sup>*Florida State University, Tallahassee, FL, United States;* <sup>2</sup>*Chemical Engineering, Florida State University, Tallahassee, FL 32310, United States*

We report experiments on a simple shear flow of a model shear banding wormlike micellar solution with a custom-built Taylor-Couette (TC) cell. The wormlike micellar solution contains cetyltrimethyl ammonium bromide (CTAB) and sodium salicylate (NaSal). Rheological measurements indicate formation of a shear stress plateau for this system at room temperature. Transient evolution of the velocity profile is investigated from rest using a step shear protocol. Shear stress experiences an overshoot followed by an undershoot and finally steady state. We report, for the first time, formation of an elastic recoil with negative velocities in this shear banding system as stress decays toward steady state. The steady state velocity profile in  $r$ - $\theta$  plane of the TC cell confirmed formation of a shear banded velocity profile with no wall-slip at the moving boundary and the proportion of the high shear band compared well with the lever rule. However, we report formation of a significant wall-slip at the stationary outer wall.

## Tuesday Afternoon

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Tuesday 1:30 Galleria I

SC19

#### **Shear-tunable colloidal gels with embedded granular particles**

Yujie Jiang, John Royer, and [Wilson Poon](#)

*School of Physics and Astronomy, The University of Edinburgh, Edinburgh, United Kingdom*

While there has been considerable progress describing single-component particulate suspensions, our understanding of heterogeneous, multi-component suspensions remains far less developed, even though most industrial suspensions fall in the latter category. Here we explore the binary suspensions composed of non-Brownian repulsive particles embedded in a colloidal gel of smaller, attractive particles. Using a novel model system where we can both index match the particles and tune their interactions, we image these binary suspensions with a confocal-rheometer in order to simultaneously access the rheology and microstructure. While individually the repulsive granular particles shear thicken and the attractive colloidal particles form a yield stress gel, the combined binary suspensions exhibit a complex, history dependent rheology. This history-dependence originates from the interplay between the large particles and the structure of the colloidal gel. At high shear rates the colloidal gel breaks up and disperses among the large particles, resulting in a strong percolated gel network upon shear cessation. However, at moderate shear rates the large particles cause the colloidal gel to phase separate into compact, disjoint clusters, dramatically decreasing the modulus of the composite below that of the un-filled gel. This behaviour is reversible, so that a collapsed composite can be rejuvenated under high shear or a strong composite can be weakened under moderate shear, giving these binary suspensions a uniquely tunable microstructure and rheology.

Tuesday 1:55 Galleria I

SC20

#### **Colloidal elasticity arises from packing of locally glassy clusters**

[James Swan](#)<sup>1</sup>, Zsigmond Varga<sup>1</sup>, Eric M. Furst<sup>2</sup>, Michael J. Solomon<sup>3</sup>, Lilian C. Hsiao<sup>4</sup>, and Kathryn Whitaker<sup>5</sup>

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Colloidal gels formed by arrested phase separation are widely found in agriculture, biotechnology, and advanced manufacturing; yet, the emergence of elasticity and the nature of the arrested state in these abundant materials remains unclear. Here, integrated experimental, computational, and graph theoretic approaches are used to understand the arrested state and the micro-structural origins of the elastic response via a model colloidal gel enabling combined measurements of the rheology, structure, and particle interactions as well as large-scale dynamic simulations. The experiments and simulations agree quantitatively in both the elastic modulus of the gel and the micro-structural correlation length as a function of strength of inter-particle attraction. To determine the micro-structural source of elasticity, the SIS-balanced graph partition is used to divide the simulated gels into minimally inter-connected clusters that act as rigid, load bearing units. We find that the number density of cluster-cluster connections grows with increasing inter-particle attraction, and explains quantitatively the emergence of elasticity in the network through the classic Cauchy-Born theory for elasticity. The graph decomposition provides further insight into the structure of the clusters -- they are amorphous -- and with increasing inter-particle attraction, the concentration of colloids internal to the clusters decreases. This internal cluster concentration maps onto the known attractive glass line of sticky colloids at low inter-particle attraction strengths and extends this glass line to higher strengths and lower particle volume fractions. The load bearing clusters in these thermodynamically unstable suspensions are arrested by a glass line, and the elasticity of the gel is the result of just a few weak contacts between these locally arrested, glassy clusters.

Tuesday 2:20 Galleria I

SC21

#### **Dynamics and flow instabilities in sheared colloidal rod gels**

[Mohan Das](#) and George Petekidis

*IESL, FORTH, Heraklion, Greece*

Gelation is the process where attractive particle interaction leads to changes in dynamical and rheological behavior of colloidal suspensions. At sufficiently high particle concentrations the suspension behavior changes from liquid-like to solid-like and the particles are trapped in a non-ergodic state. Colloidal rod gels share many similarities with their spherical counterparts, albeit notable differences exist in the suspension microstructure, phase behavior (e.g. liquid crystallinity), single particle dynamics and flow behavior owing to their high aspect ratio. Here we present the study of dynamics and mechanical properties of attractive colloidal rod suspensions. Silica rods ( $L = 4.5 \mu\text{m}$ ,  $L/D = 10$ ) suspended in 65 wt% CsCl solution is used as a model system to understand colloidal rod gel behavior at microscopic scale. We used a stress controlled rheometer in conjunction with bright-field and confocal microscopy to observe changes in suspension microstructure at different length scales

during linear and nonlinear rheological measurements. Furthermore, we carried out 3D particle tracking to follow single rod dynamics under equilibrium and non-equilibrium conditions. Step-rate measurements show irreversible formation of macroscopic vorticity aligned dense particle clusters that show “log-rolling” behavior. We probe the relation between this phenomenon and confinement by varying the gap in rheometer geometry. We propose a phase diagram based on particle volume fraction and Peclet number to identify the log rolling regime. Finally, experimental results are compared with results obtained from computer simulations\*, taking into account both Hydrodynamic interactions and confinement effects.

\*Work in collaboration with Z. Varga and J. Swan, Department of Chemical Engineering, MIT, USA.

Tuesday 2:45 Galleria I

SC22

### **Controlling the rotational dynamics of semiflexible colloidal chains**

Steve Kuei and Sibani Lisa Biswal

*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Semiflexible filaments deform in response to external forces and their surrounding fluid. When a simple rotating force field is applied, the resulting dynamical response can range from constant rotary orbits to complicated non-reciprocal orbits; the latter, in particular, have significant potential for microfluidic scale propulsion and fluid manipulation. External driving forces, hydrodynamic drag forces, and elastic restoration forces act along the length of the filament, and compete to generate these rich dynamics, but their exact impact, and if they allow us to tune the dynamical response, is still unclear. We study this system using paramagnetic colloidal particle chains and a rotating magnetic field as an external force, experimentally probing the various dynamical regimes as a function of the dimensionless Mason and magnetoelastic numbers. In particular, we focus on the non-reciprocal dynamics where the chains beat with a periodic deformation, or form tightly wrapped coils. By complementing our studies with Brownian dynamics bead-spring simulations, we work towards a more complete understanding and control of fiber dynamics.

Tuesday 3:45 Galleria I

SC23

### **Nonlinear viscoelasticity of a dilute suspension of Brownian spheroids in oscillatory shear flow**

Toni M. Bechtel and Aditya S. Khair

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

The nonlinear viscoelasticity of a dilute suspension of Brownian spheroids subject to an oscillatory shear deformation is calculated numerically. This is achieved by determining the suspension microstructure, parameterized via the orientation distribution function. Specifically, the long-time periodic orientation distribution function is obtained via a numerical solution to the Fokker-Planck equation. From an ensemble average of the particle stresslet, the entire stress tensor and relevant birefringence parameters, namely the average orientation angle and linear dichroism, are calculated; this is done over a range of Weissenberg number ( $Wi$ ) and Deborah number ( $De$ ). Detailed calculations are presented for prolate spheroids of aspect ratio  $r = 20$ . We provide results in four viscoelastic regimes: linear viscoelastic ( $Wi \ll 1$ ); quasi-linear viscoelastic ( $Wi > 1$  and  $Wi/De \ll 1$ ); quasi-steady viscoelastic ( $De \ll 1$ ); and finally the nonlinear viscoelastic regime ( $Wi > 1$  and  $Wi/De > 1$ ), which is our main emphasis. In this last regime, where the nonlinear and unsteady viscoelasticity of the material is probed, multiple overshoots are observed in the shear stress and first normal stress difference. The mechanistic origin of these overshoots can be understood from the periodic orientation dynamics (i.e. Jeffery orbits) of a particle under steady shear in the absence of Brownian rotation ( $Wi \ll 1$ ). This is achieved by simultaneously analyzing the microstructure, shear stress, first normal stress difference, and birefringence parameters specifically at  $Wi = 20$  and  $De = 1$ . For these values of  $Wi, De$ , and  $r$ , the period of a Jeffery orbit is comparable to the period of an oscillation cycle, allowing sufficient time for a single Jeffery orbit (and subsequent overshoot) to occur during an oscillation cycle. We contrast this behavior to recent work by Khair (JFM 2016) on nearly spherical particles, for which many more overshoots are observed during an oscillation cycle, due to the shorter period of the Jeffery orbit.

Tuesday 4:10 Galleria I

SC24

### **LAOS response of the rigid-rod model in nematic regime**

Marco De Corato<sup>1</sup> and Giovanniantonio Natale<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Imperial College London, London, United Kingdom;* <sup>2</sup>*University of Calgary, Calgary, Canada*

Nematic phase of rigid-rod molecules presents rheological complexities given the intrinsic anisotropy of the molecules and spatial variation of an average molecular orientation (director) in the bulk. The Doi-Hess rigid-rod<sup>1,2</sup> model has been shown to predict correctly the rheological response and orientation dynamic of nematic phase. This microscopic model has been investigated in simple shear and elongational flow. In simple shear flow, the dynamic response was demonstrated to be quite complex and depending on the interplay between the intensity of the excluded volume potential and the applied shear flow different dynamics are obtained (log-rolling, wagging and tumbling regimes). Oscillatory shear flow is a model transient flow field which introduces a transient and periodic perturbation to the system. Recently, large amplitude oscillatory shear (LAOS) has attracted interest given the rich rheological response that is obtained. This enables more precise and complete characterization of the complex materials. However, the interpretation at the microstructural level of the LAOS response is still limited to specific systems. For the first time, we aim to investigate the response of the rigid-rod model in oscillatory shear flow. We perform numerical simulations of the Doi-Hess kinetic equation using Brownian dynamics and an expansion in spherical harmonics. The results show that the orientation tensor (second order moment of the orientation distribution) response for this system contains even and odd modes in the Fourier space. Finally, we attempt to link microstructural information to the rheological response for this system.

<sup>1</sup> Hess, S. (1976). *Zeitschrift für Naturforschung A*, 31(9), 1034-1037. <sup>2</sup> Masao, D. (1981). *Journal of Polymer Science: Polymer Physics Edition*, 19, 243.



Tuesday 4:35 Galleria I

SC25

**Short and soft nanocylinders: Multi-domain structure and tunable rheology**Daniele Parisi<sup>1</sup>, Ying-Bo Ruan<sup>2</sup>, Chen-Yang Liu<sup>2</sup>, Benoit Loppinet<sup>3</sup>, and Dimitris Vlassopoulos<sup>1</sup><sup>1</sup>Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece; <sup>2</sup>Institute of Chemistry, Chinese Academy of Sciences, Beijing, China; <sup>3</sup>Institute of Electronic Structure and Laser, FORTH-IESL, HERAKLION, Greece

Whereas static and dynamic properties of cylinders with large aspect ratio ( $L/D > 10$ ) have been extensively investigated, much less is known for short cylinders ( $L/D < 10$ ). Only recently, simulations and experiments have shown complexities associated with the isotropic-to-liquid crystalline phase transition in short cylinders, where particles kinetically arrested into macroscopic multi-domain structures before eventually arranging into a smectic phase. Additionally, the role of softness on structure and dynamics, well established for spherical colloids, is unexplored for short nanocylinders. In this experimental work we introduce a new model system of short and soft (grafted) cylinders ( $L/D = 6$ ) in order to link structure, softness and dynamics by combining SAXS, DLS, visual observations and different rheological techniques: piezo rheometry for high frequencies ( $> 100$  rad/s), standard frequency sweeps (0.01 to 100 rad/s) and creep to extend the low frequency region. We find an unprecedentedly rich rheological response embracing a broad range of concentrations, from dilute to nearly melt state. An isotropic liquid gives rise to an isotropic multi-scale structure with local orientation, to an arrested state and finally to a hexagonally packed arrangement. These states exhibit distinct rheological signatures, encompassing polymer layer and colloidal responses, which we discussed in detail, in the linear and nonlinear regime. We argue that this class of nanocolloids with softness and short-ranged orientational order offer new possibilities for tailoring flow properties of suspensions.

Tuesday 5:00 Galleria I

SC26

**Dynamics and rheology of suspensions of particles with arbitrary shapes**Mingyang Tan<sup>1</sup> and Travis W. Walker<sup>2</sup><sup>1</sup>School of Chemical, Biological, and Environmental Engineerin, Oregon State University, Corvallis, OR 97321, United States;<sup>2</sup>Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, rapid city, SD 57701, United States

Suspensions of particles in a fluid medium are ubiquitous in natural substances, such as proteins, bacteria, and viruses in biological media, and in engineering fields, such as precursors of composite materials, dispersions of pigments in paint, and mixtures of polymer emulsions. While the non-equilibrium properties of suspensions of spherical particles have been widely studied, suspensions of aspherical particles create new questions and phenomena that still need to be explained. The non-equilibrium properties require an accurate knowledge of the interactions among particles, i.e., hydrodynamic interaction and/or other external forces. The hydrodynamic interactions depend on the configuration of the suspension, which makes itself formidable to calculate for a suspension of aspherical particles, caused by the complex geometry. In this study, we decomposed the aspherical particles into constitutive spheres and constrained them in rigid-body assemblies. We use Stokesian dynamics to model and study the dynamics of the rheology of the suspension, and we apply this method to any arbitrarily-shaped particles.

**Symposium PM****Polymer Melts: From Molecular Rheology to Processing**

Organizers: Reza Foudazi and Richard Graham

Tuesday 1:30 Plaza I

PM6

**Rheology of molten polyolefin interfaces: Slip in shear, strain hardening in extension**Alex M. Jordan<sup>1</sup>, Kyungtae Kim<sup>2</sup>, Bongjoon Lee<sup>2</sup>, Ean Ludtke<sup>2</sup>, Frank S. Bates<sup>2</sup>, Christopher W. Macosko<sup>2</sup>, and Olivier Lhost<sup>3</sup><sup>1</sup>Polymer Engineering, University of Wisconsin - Stout, Menomonie, WI 54751, United States; <sup>2</sup>Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, United States; <sup>3</sup>Total, Feluy, Belgium

While isotactic polypropylene (iPP) and polyethylene (PE) are chemically similar, they are immiscible in the melt state and possess poor interfacial adhesion in the solid state. Here, we focus on the use of rheology to understand the iPP/PE interface in the melt. Using Ziegler-Natta catalyzed high density polyethylene (zHDPE) and isotactic polypropylene (ziPP) as well as single-site (metallocene) catalyzed high density polyethylene (mHDPE), linear low density polyethylene (mLLDPE), and isotactic polypropylene (miPP) we produced a range of multilayer films. Films with 2 layers, 160 layers, and 640 layers were fabricated via multilayer coextrusion using ziPP/zHDPE, mHDPE/miPP, and mLLDPE/miPP. In startup of steady shear the Ziegler catalyzed pair showed interfacial slip at  $\sim 10$  kPa, well below the critical shear stress threshold for disentanglement.1 The interfacial slip at low shear stress was likely due to the build-up at the interface of low molecular weight oligomers that were below the entanglement molecular weight of iPP and PE. Interestingly the Ziegler catalyzed pair also displayed the lowest interfacial adhesion in the solid state, which was attributed to oligomer build-up at the interface.2 Conversely, using extensional rheology we observed strain hardening in the multilayers of the single-site catalyzed pairs, first with the miP/mLLDPE system at 160 layers. At 640 layers, effectively quadrupling the interfacial area in multilayer films, the strain hardening behavior became more pronounced in the mLLDPE/miPP system and strain hardening emerged in the mHDPE/miPP system, even though no strain hardening was observed in control mHDPE, mLLDPE, and miPP films. We correlate this strain hardening behavior with the narrow polydispersity of these single -site catalyzed polyolefins resulting in a high degree of chain entanglements in the melt interface.

References: 1. P. C. Lee, et al., J. Rheol., 2009, 53, 893-915.; 2. A. M. Jordan, et al., Macromolecules, 2018, 51 (7), 2506-2516.

Tuesday 1:55 Plaza I

PM7

**Elongational rheology of unentangled polystyrene and poly(tert-butyl styrene) melts**Hiroshi Watanabe and Yumi Matsumiya*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

Viscoelastic relaxation of polymers is insensitive to their chemical structure and thus universal under shear, but this universality vanishes under elongation. This study conducted elongational rheological measurements for unentangled melts of narrow MWD polystyrene (PS) and poly(tert-butyl styrene) (PtBS) having nearly the same number of Kuhn segments (~ 30) per chain. Both materials exhibited strain-hardening followed by strain-softening on an increase of the Weissenberg number to and above unity, and the strain-hardening was stronger for PtBS. These findings were analyzed in relation to the FENE effect and orientation/stretch-induced reduction of the segmental friction with the aid of the FENE-PM model. The analysis suggested that the magnitude of friction reduction is not uniquely determined by the stress reflecting the chain conformation at each moment but exhibits retardation possibly due to retarded adjustment of orientation/stretch to the environment.

Tuesday 2:20 Plaza I

PM8

**Interdiffusion of two molten polystyrenes under SAOS**Wissam Nakhle<sup>1</sup>, Paula M. Wood-Adams<sup>2</sup>, and Marie-Claude Heuzey<sup>3</sup><sup>1</sup>*MIAE, ENCS, Concordia University, Montreal, QC H3G 2B7, Canada;* <sup>2</sup>*Chemical Engineering, ENCS, Concordia University, Montreal, Quebec H3G 1M8, Canada;* <sup>3</sup>*Crepec, Chemical Engineering, Polytechnique Montreal, Montreal, QC H3C3A7, Canada*

This paper reports on the characterization of interdiffusion at the interface between two molten polystyrenes, under small amplitude oscillatory shear. SAOS measurements are sensitive to composition changes, which makes them suitable to examine polymeric interdiffusion. The main objectives are to measure polymeric interdiffusion experimentally, to assess the effect of SAOS and frequency, and to determine the diffusion coefficient in a molten binary polystyrene system from SAOS measurements. Binary polystyrene interdiffusion is studied at 190°C using a rotational rheometer and the diffusion coefficient is evaluated at various oscillation frequencies. Under SAOS, polymer molecules are in quasi-equilibrium, and the measured torque remains constant in homogeneous samples, during time sweeps at constant frequency. The SAOS torque-time curve obtained from concentric binary samples, is dependent on composition and reflects the interdiffusion dynamics. An interdiffusion model based on the mean-field theory is used to describe the composition profile, and a non-linear mixing rule is used to describe the effect of composition on the complex viscosity. The SAOS torque-time curve at constant frequency carried out on a concentric binary specimen, is resolved in combination with the theory of linear viscoelasticity. The study will show that such measurements can be used to determine the diffusion coefficient, and that the diffusion rate is increased by oscillatory motion in the linear viscoelastic regime.

Tuesday 2:45 Plaza I

PM9

**Determining the dilution exponent for 1,4-polybutadienes using blends of entangled monodispersed star with unentangled, low molecular weight linear polymers**Ryan Hall<sup>1</sup>, Beomgoo Kang<sup>2</sup>, Sanghoon Lee<sup>3</sup>, Taihyun Chang<sup>3</sup>, David Venerus<sup>4</sup>, Nikos Hadjichristidis<sup>5</sup>, Jimmy Mays<sup>2</sup>, and Ronald G. Larson<sup>6</sup><sup>1</sup>*Macromolecular Science and Engineering Program, University of Michigan, Ann Arbor, MI 48197, United States;* <sup>2</sup>*University of Tennessee, Knoxville, TN, United States;* <sup>3</sup>*Chemistry, Pohang University of Science and Technology, Pohang, Republic of Korea;* <sup>4</sup>*Chemical and Biological Engineering, Illinois Institute of Science and Technology, Chicago, IL, United States;* <sup>5</sup>*Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, KAUST, Thuwal, Saudi Arabia;* <sup>6</sup>*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States*

We determine experimentally the “dilution exponent”  $\alpha$  for entangled polymers from the scaling of terminal time with entanglement density from the linear rheology of three well characterized 1,4-polybutadiene 4-arm star polymers. These stars are blended with low-molecular-weight, unentangled linear 1,4-polybutadiene at various star volume fractions,  $\phi_s$ . Assuming only that the rheology of monodisperse stars depends solely on the plateau modulus  $G_N^0(\phi_s) \propto \phi_s^{1+\alpha}$ ; the number of entanglements per chain  $M_e(\phi_s) \propto \phi_s^{-\alpha}$ ; and the tube-segment frictional Rouse time  $\tau_e(\phi_s) \propto \phi_s^{-2\alpha}$ , we show that only an  $\alpha=1$  scaling superposes the  $M_e(\phi_s)$ -dependence of the terminal cross-over frequency  $\omega_{x,t}$  of the blends with those of pure stars, while an order-of-magnitude deviation between these dependencies is found if one takes  $\alpha=4/3$ . The nearly exponential dependence of  $\omega_{x,t}$  on  $M_e(\phi_s)$  is strong enough to clearly distinguish the value of the dilution exponent  $\alpha$ , which is not possible from the weaker dependence of the low-frequency cross-over modulus  $G_{x,t}$  on  $M_e(\phi_s)$ . We show that this conclusion holds when accounting for experimental uncertainties in arm molecular weights. This is the first clear rheological determination of  $\alpha$  that does not rely on the use of any particular tube model, but only on the dependence of rheology on the above three parameters. We also show that a generalized tube model, the “Hierarchical model”, using the “Das” parameter set with  $\alpha = 1$  performs reasonably in predicting the terminal and plateau regions of the melts and blends featured here.

Tuesday 3:45 Plaza I

PM10

**Mobility of polymer-tethered nanoparticles in unentangled polymer melts**Ting Ge and Michael Rubinstein*Mechanical Engineering and Materials Science, Duke University, Durham, NC 27710, United States*

A scaling theory is developed for the motion of a polymer-tethered NP in an unentangled polymer melt. Both NPs tethered with a single polymer chain (tail) and with multiple chains (tails) are studied. For a single-tail NP in a polymer melt, we identify two types of scaling regimes, particle-

dominated and tail-dominated regimes, depending on the NP diameter  $d$  and the size of the tail  $R_{tail}$ . In a particle-dominated regime, the single-tail NP motion is dominated by the bare NP, as the friction coefficient of the tail is lower than that of the less mobile particle. In a tail-dominated regime, the single-tail NP motion is dominated by the tail when the tail friction coefficient surpasses that of the particle at time scales above a crossover time. A multi-tail NP in an unentangled polymer melt is studied by considering a corresponding star polymer in the same melt. For loosely grafted tails, the boundary separating the tail-dominated and particle-dominated regions in the  $(d, R_{tail})$  parameter space is similar to but shifted with respect to that for a single-tail NP. In each tail-dominated regime, the crossover time is smaller than its counterpart for a single-tail NP, resulting from enhanced effects of the multiple tails. For densely grafted tails, a multi-tail NP diffuses through the polymer melt with the hydrodynamic radius equal to the radius of the corresponding star polymer.

Tuesday 4:10 Plaza I

PM11

### **A simple constitutive model for polymer blends: Predictions and experimental comparisons for viscometric and non-viscometric flows**

Joseph D. Peterson<sup>1</sup>, Victor Boudara<sup>2</sup>, Daniel J. Read<sup>2</sup>, Chandi Sasmal<sup>3</sup>, and L. Gary Leal<sup>1</sup>

<sup>1</sup>University of California, Santa Barbara, Santa Barbara, CA 93106, United States; <sup>2</sup>School of Mathematics, University of Leeds, Leeds, West Yorkshire LS29JT, United Kingdom; <sup>3</sup>Department of Chemical Engineering, Indian Institute of Technology, Ropar, Rupnagar, punjab 140001, India

Industrially relevant flows of industrially relevant polymers are notoriously difficult to model; the polymers are compositionally complex (comprising a broad spectrum of chain lengths and chain architectures), and the flow fields are non-viscometric and non-linear. In this talk, we share our recent progress in the constitutive modelling of polydisperse melts of linear chain polymers. Our constitutive model is a simple construct free of adjustable parameters, derived as an amalgam of double reptation (a temporary network approximation for polydisperse melts) and Rolie Poly (a simplified tube model for monodisperse melts), and is suitable for CFD modelling applications. We present the predictions of this model in viscometric flows (start-up of steady shear and uniaxial extension) and non-viscometric flows (2D contraction/expansion through a slit) and compare against experimental findings of the same.

Tuesday 4:35 Plaza I

PM12

### **Computer simulations and experimental measurements of extrudate swell for linear polystyrenes**

Ben Robertson<sup>1</sup>, Thomas C. McLeish<sup>2</sup>, and Richard L. Thompson<sup>1</sup>

<sup>1</sup>Department of Chemistry, Durham University, Durham, County Durham DH12LF, United Kingdom; <sup>2</sup>University of York, York, United Kingdom

We describe the finite element simulation and experimental studies of extrudate swell in a range of model polystyrenes. Calculations use the tube model based Rolie-Poly constitutive equation to predict extrudate swell for a range of linear polystyrenes. We present isothermal extrusion experiments on the same polymers and can obtain good predictions well into the strong chain stretching regime. The predictions for swelling ratios match the experimental results up to Rouse Weissenberg numbers of 7. An over-prediction in extrudate swell is seen above this point, especially in the case of monodisperse melts, consistent with the reduction in monomeric friction at high monomer alignment proposed by others. We incorporate a simple form for reduction of monomeric friction into the Rolie-Poly equation and show that improved predictions of extrudate swell at higher rates can be obtained for monodisperse and polydisperse systems.

Tuesday 5:00 Plaza I

PM13

### **Nonlinear shear rheometry of melts and concentrated solutions of polymers with varying molecular structure**

Salvatore Costanzo<sup>1</sup>, Daniele Parisi<sup>2</sup>, and Dimitris Vlassopoulos<sup>3</sup>

<sup>1</sup>Univ. of Montpellier, Montpellier, France; <sup>2</sup>Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece; <sup>3</sup>Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece

We report on recent efforts to improve rheometric capabilities for polymer melts (mostly entangled but also some unentangled) and concentrated solutions. Using a modular cone-partitioned plate geometry it is relatively straightforward to determine shear stress,  $N1$  and  $N2$ , over a wide range of Rouse-Weissenberg numbers, exceeding the value of 40, well into the stretching regime. For well-characterized linear polymers (mainly polystyrene) we identify stretching and tumbling regimes, compare with current state-of-the-art modeling and simulations, as well as with results from neutron scattering measurements with quenched samples at selected shear rates. With this background, we explore the effects of macromolecular architecture and address in particular the nonlinear shear rheology of star and ring polymers (again, well-characterized) and their mixtures with linear polymers. Particular emphasis is put on comparing with linear polymers, as well as existing predictions from theoretical modeling and simulations, focusing on scaling laws and the Cox-Merz rule.

## Symposium PG Polyelectrolytes, Self-assembling Systems & Gels

Organizers: Nick Virgilio and Lilian Hsiao

Tuesday 1:30 Bellaire

PG1

### **Gelation mechanism of tri- and penta-block copolymers in the presence of small molecules**

Michelle A. Calabrese<sup>1</sup>, Rong Yang<sup>2</sup>, Bradley D. Olsen<sup>1</sup>, and Daniel S. Kohane<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States;* <sup>2</sup>*Boston Children's Hospital, Boston, MA, United States*

Treatments for ear diseases typically require high-dose oral drug administration. Until recently, direct treatment through the tympanic membrane (TM) to the middle ear was not possible. We have developed a temperature-responsive block copolymer system which is liquid at room temperature but gels in contact with the warm TM, which has achieved non-invasive and sustained drug delivery across the TM. The formulation consists of either a triblock copolymer (Pluronic-407, P407) or pentablock copolymer (P407-polybutylphosphoester, PBP), a drug, and three small molecule chemical permeation enhancers (CPEs) that facilitate drug transport across the TM. The mechanism for this reversible gelation process, tuned by the different polymer architectures and the presence of CPEs, drastically differs between the two formulations, resulting in different clinical efficacy. In the P407 formulation, CPE addition weakens the elastic modulus during gelation, reducing efficacy. However, upon modifying the polymer with hydrophobic endblocks, the resulting PBP formulation shows enhanced gelation with CPE addition. Using x-ray scattering, contrast variation neutron scattering, and rheology, we demonstrate that morphological differences result between the systems during heating that explain the differences in gelation behavior. In P407, FCC structures form and the CPEs concentrate within the micelle core. The micelle size and lattice spacing systematically increase with CPE addition, weakening the elastic modulus. In PBP, however, disordered, bridged micelles form due to the endblock hydrophobicity; this bridging strengthens the modulus. Here, the CPEs are more uniformly distributed than in P407, and the micelles remain closely packed and highly bridged with CPE addition. This fundamental understanding of the gelation mechanisms and roles played by additives during block copolymer self-assembly may enable the rational design of temperature-responsive drug delivery systems that can overcome biological barriers.

Tuesday 1:55 Bellaire

PG2

### **Surfactant-activated microgels: A pathway to viscoplastic gels**

Sarah Goujard<sup>1</sup>, Clémentine Locatelli-Champagne<sup>2</sup>, Jean-Marc Suau<sup>2</sup>, and Michel Cloitre<sup>1</sup>

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Stimuli-responsive microgels are colloidal particles made of cross-linked polymeric networks that undergo a volume transition in response to changes in pH, temperature, or solvent quality. As particle swelling provokes a dramatic increase of the volume fraction, randomly close-packed suspensions with remarkable viscoplastic properties and optical transparency, can be obtained at very low polymer content. These features are exploited to design rheological modifiers used in cosmetics, pharmaceuticals, and food products.

A wide-spread trigger of microgels in industrial applications is pH. Crosslinked acrylic acid or alkyl acrylate/methacrylic acid microgels swell by a large amount when the carboxylic functions borne by the polymer network are ionized. In general pH-sensitive microgels suffer from a great sensitivity to ionic strength variations and to the fact that the optimum rheology is reached at high pH, which is detrimental to their use in personal care products.

Here we explore a strategy that consists in triggering the swelling of microgels by the addition of guest molecules such as surfactants or oligomers, which adsorb onto the polymeric network and induce swelling. The great challenge is to control and model the volume transition and the rheological properties in terms of enthalpic and entropic interactions that develop between the polymeric network and the guest molecules. We address this question for alkyl acrylate/methacrylic acid copolymers which are activated by neutral or ionic surfactants. Using rheology, fluorescence techniques, and SAXS investigations we elucidate the microscopic mechanisms that connect the composition of microgel/surfactant mixtures to rheological properties such as the yield stress and the shear thinning behaviour. In addition to providing exquisite solutions to the design of new rheology modifiers for personal care products, this host-guest paradigm opens the route to other applications, for instance to adsorb toxic residues from complex formulations.

Tuesday 2:20 Bellaire

PG3

### **Longtime viscoelasticity of soft bottlebrush gels**

Liheng Cai

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Gels formed by crosslinking bottlebrush polymers are often free of entanglements. As such, the stiffness of bottlebrush gels can be precisely controlled by tuning the concentration of crosslinks to match that of soft biological objects. However, much less is understood about the viscous moduli of bottlebrush gels, particularly at longtime scales comparable to the dynamic behavior of cells and tissues. Here, we develop means to synthesize bottlebrush gels and study their longtime viscoelasticity using bulk rheology. We discover a time-dependent viscous modulus governed by the dynamics of dangling bottlebrush polymers. While without forming entanglements, these polymers are confined by network meshes and exhibit dynamics similar to arm-retraction of entangled branched linear polymers. Our study provides new insights in designing soft bottlebrush

gels with independent control over elastic and viscous moduli, and such gels can be used to elucidate the roles of viscous modulus in cell-substrate interactions.

Tuesday 2:45 Bellaire

PG4

### **Signatures of physical aging in Carbopol microgel**

Mayank Agarwal and Yogesh M. Joshi

*Chemical Engineering, Indian Institute of Technology Kanpur, KANPUR, UTTAR PRADESH 208016, India*

An aqueous suspension of Carbopol, also known as Carbopol microgel has a paste-like consistency and demonstrates a presence of yield stress. There is an ongoing debate in the literature whether Carbopol microgel undergoes physical aging. In this work, we perform oscillatory shear and creep experiments on 0.2 weight % Carbopol - 940 microgel. It is observed that imposition of oscillatory strain field in a linear regime to a shear rejuvenated Carbopol microgel leads to very weak enhancement in elastic modulus as a function of time. The creep experiments are carried out at different aging times after stopping the rejuvenation and at different stress magnitudes below and above the yield stress. It is observed that the strain induced in the microgel decreases with increase in the aging time at which the creep stress was applied. The transformation of the creep data to the effective time domain, wherein real time is normalized by perceived aging time-dependent relaxation time, leads to time-aging time superposition of the creep data. On the other hand, this exercise also suggests relaxation time to show a power-law dependence on aging time. We observe that the power law index that has value around 0.7 in a limit of small stresses, decreases with stress and tends to zero in the limit of yield stress. This study, therefore, suggests that similar to various other soft glassy materials, the Carbopol microgel indeed shows physical aging whose intensity weakens with stress as the stress approaches the yield stress.

Tuesday 3:45 Bellaire

PG5

### **Characterization of the change in rheological properties of a fibrous colloidal gel due to consecutive phase transitions and sample preparation**

Matt Wehrman<sup>1</sup>, Seth Lindberg<sup>2</sup>, and Kelly Schultz<sup>1</sup>

<sup>1</sup>*Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States;* <sup>2</sup>*Procter and Gamble, West Chester, OH 45069, United States*

Colloidal gels are used as rheological modifier in fabric, home care and consumer care products. Of concern in product design is whether processing history, including shear stress, changes the material properties. To assess this, we characterize a hydrogenated castor oil colloidal gel (HCO) during consecutive phase transitions using  $\mu^2$ rheology, microrheological characterization in a microfluidic device. HCO is a colloidal fiber that undergoes a phase change in response to an osmotic pressure gradient. The microfluidic device designed for this work enables exchange of the fluid environment around a sample with minimal sample loss or addition of shear stress. After fluid exchange in the device, the rheological evolution of HCO material properties is characterized with multiple particle tracking microrheology (MPT). In MPT, fluorescent probe particles are embedded in the material and the Brownian motion of these particles is measured to determine rheological properties. Two HCO sample are measured with  $\mu^2$ rheology, a presheared 0.125 wt% HCO solution and an unsheared 4 wt% HCO gel. In both samples, HCO returns to the same equilibrium properties after each phase transition, but these equilibrium properties differ between the two sample preparations. Therefore, sample preparation is changing the rheological properties of the material and also suggests changes in the sample structure. When comparing our measurements with previous work by Wilkins, Spicer and Solomon, the rheology suggest that during gelation the presheared HCO solution cannot form an entangled network structure. During degradation, the unsheared HCO gel cannot degrade into single colloids in solution. From these results, we conclude that the equilibrium rheological properties and material microstructures depend on the shear history of the starting material, which has important implications in end use products made with colloidal gel scaffolds.

Tuesday 4:10 Bellaire

PG6

### **The role of network topology in soft gels**

Minaspi Bantawa<sup>1</sup>, Mehdi Bouzid<sup>2</sup>, and Emanuela Del Gado<sup>1</sup>

<sup>1</sup>*Georgetown University, Washington, DC, United States;* <sup>2</sup>*LPTMS, Universite Paris Sud, Paris, France*

Soft gels formed by the self-assembly of systems like colloids, proteins and polymers into poorly connected networks are ubiquitous in nature. Despite their importance in a wide range of industrial applications with tunable mechanical properties, the fundamental understanding of how the microstructure determines the mechanical response is still not sufficient. Here we investigate the role of network topology and of frozen-in stresses in a model gel through 3-D simulations. Our study links the topology of the network organization in space to the stress redistribution under shear and to the characteristics of its linear viscoelastic spectrum. Furthermore, for a fixed topology, we investigate the role of pre-stresses and of the bending stiffness of the gel fibers in the nonlinear response, the damage and the brittleness of the networks.

Tuesday 4:35 Bellaire

PG7

### **Tuning the structure and rheology of nanoemulsion colloidal gels through screening of electrostatic interactions and thermoresponsive polymer bridging**

Li-Chiun Cheng<sup>1</sup>, Signe Lin Kuei Vehusheia<sup>2</sup>, and Patrick S. Doyle<sup>3</sup>

<sup>1</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>ETH Zürich, Zurich, Switzerland; <sup>3</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States

Self-assembly of colloidal gels is intimately related to the interparticle potential. Particle attraction triggered by thermally-responsive polymer bridging is a powerful method to externally modulate the interparticle potential in time and thus finely control the resulting arrested states. It is desirable to design systems which are responsive to multiple stimuli for refined material property control and advanced applications. In this work, we study the rheological properties and the microstructures of a model oil-in-water nanoemulsion system developed by our group where the aggregation of the droplets is controlled by the interplay of inter-droplet polymer bridging, depletion attraction, and electrostatic repulsion. The nanoemulsion system allows us to independently trigger the colloidal self-assembly by varying the ionic strength and/or the temperature. We carefully manipulate the interparticle potentials through depletion attraction, electrostatic repulsion and interdroplet bridging. We show how sequential application of external stimuli can be used to tune rheological properties and microstructures. We also provide a molecular understanding of the underlying mechanisms at play.

Tuesday 5:00 Bellaire

PG8

### **From well-entangled to partially-entangled wormlike micelles: A characterization by rheological modeling, diffusing wave spectroscopy, and small-angle neutron scattering**

Weizhong Zou<sup>1</sup>, Grace Tan<sup>1</sup>, Hanqiu Jiang<sup>2</sup>, Karsten Vogtt<sup>2</sup>, Michael R. Weaver<sup>3</sup>, Peter Koenig<sup>3</sup>, Gregory Beaucage<sup>2</sup>, and Ronald G. Larson<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States; <sup>2</sup>University of Cincinnati, Cincinnati, OH, United States; <sup>3</sup>Procter & Gamble, Mason, OH, United States

We use mechanical rheometry and diffusing wave spectroscopy (DWS) along with small angle neutron scattering (SANS), combined with a mesoscopic simulation model, the "pointer algorithm," to obtain characteristic lengths and time constants for wormlike micelle (WLM) solutions over a range of surfactant and salt concentrations encompassing the transition from unentangled to entangled solutions. The solutions contain both sodium lauryl ether sulfate (SLEIS) and cocoamidopropyl betaine (CAPB), and a simple salt (NaCl). The pointer algorithm is extended to allow fast relaxation of unentangled micelles; thereby micelle length, breakage rate and entanglement and persistence lengths can be extracted from linear rheological measurements of partially entangled WLM solutions. DWS provides the high frequency data needed to determine micelle persistence length. By fitting  $G'$  and  $G''$  to the predictions of the pointer algorithm, a rapid change in micellar length from 1 to 7  $\mu\text{m}$  is observed over a change in salt ion concentration from  $[\text{Na}^+] = 0.6\text{-}0.8\text{ M}$ , as the solution enters the well-entangled regime. The micelle lengths from SANS at a 7.5-fold smaller surfactant concentration are 0.4 to 1  $\mu\text{m}$  over a similar range of salt concentrations, roughly consistent with the values derived from rheology once the effect of the lower surfactant concentration is accounted for. The micellar persistence length from rheology (40 nm) is found to be roughly consistent with that from SANS (30 nm) at a lower surfactant concentration. This is, to our knowledge, the first time that quantitative comparisons of structural features including micelle length are made between rheology and SANS. Finally, the scaling laws for micelle diffusion and recombination times indicate that micelle kinetics are reaction controlled leading to mean-field recombination with surrounding micelles over the concentration range of interest except at very low and high surfactant concentrations where either short micelles or branched micelle clusters are dominant.

## **Symposium PS Polymers in Solution**

Organizers: Nicolas J. Alvarez and Cari Dutcher

Tuesday 1:30 Post Oak

Keynote PS19

### **Rheology of particle-laden polymeric fluids: A perspective from the order of addition**

Hao Sun

Rheology Control Platform, PPG Industries, Inc., Allison Park, PA 15101, United States

Polymeric materials serve as key components in the coatings industry. It is known that the preparation of paints is a complex process, and many factors contribute to the final coating properties. In this study, the order of addition of several key components in an automotive clear coat was varied to understand and demonstrate the impact of the formulation process. It was found that the rheological properties of these multi-component polymeric fluids depend not only on the mixture compositions, but also on the order of addition. For the system studied here specifically, it was found that the relative order between certain polymer and particulate additives plays a vital role in determining the rheological properties of the mixture. Further, NMR tests suggest a competitive interaction between each component, and shed light on the microscopic origin of the observed differences. These findings provide significant practical guidance to the manufacturing.

Tuesday 1:55 Post Oak

PS20

**Shear rheology of carbon nanotubes in chlorosulfonic acid**Ivan Rosa de Siqueira, Oliver S. Dewey, Lauren W. Taylor, Elie A. Bengio, and Matteo Pasquali*Department of Chemical & Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Carbon nanotubes (CNTs) have been widely used in the development of new materials, such as macroscopic fibers, thin films, and aerogels. The macroscopic materials with the best properties are based on liquid-phase processing of CNTs dispersed in superacids. Therefore, process optimization relies on fundamental understanding of the mechanical response and rheological behavior of these complex solutions under flow. In this work, we present an experimental study on the shear rheology of CNTs dispersed in chlorosulfonic acid (CSA). The experiments were conducted in a cylindrical Couette geometry with a setup to avoid the chemical reaction between the superacid solvent and moisture in the air. Experiments performed for different aspect ratios over a wide range of concentrations elucidate the highly non-Newtonian behavior of CNT/CSA solutions. Dynamic tests show the viscoelastic response of CNT/CSA solutions within the linear viscoelastic regime in terms of both elastic and viscous moduli. A rigorous pre-shear methodology is used together with small amplitude oscillatory tests to estimate the material relaxation time and avoid memory effects between two consecutive measurements. Furthermore, steady-state tests highlight the strong shear rate-dependent viscosity of CNT/CSA solutions under shear flows.

Tuesday 2:20 Post Oak

PS21

**Rheology of dry native cellulose in solution with ionic liquids**Nyalaliska W. Utomo<sup>1</sup>, Behzad Nazari<sup>1</sup>, Sujyot Mony<sup>1</sup>, Preet Jain<sup>2</sup>, Indira Saifuddin<sup>2</sup>, and Ralph H. Colby<sup>1</sup><sup>1</sup>*Materials Science and Engineering, The Pennsylvania State University, University Park, PA, United States;* <sup>2</sup>*Chemical Engineering, The Pennsylvania State University, University Park, PA, United States*

There has been a pursuit of good solvents to dissolve cellulose, the most abundant renewable biopolymer on Earth. Unlike most traditional solvents, certain ionic liquids (ILs) are found to have the ability to dissolve cellulose completely by breaking hydrogen bonds in cellulose chains without derivatizing it. These novel solvents have low vapor pressure and can be regenerated and reused for many process cycles. Moreover, cellulose fibers spun from IL solutions have twice the modulus of derivatized cellulose, since all the native hydrogen bonding groups that make wood strong are still present. Rheology of cellulose/IL solutions was characterized in terms of concentration, molecular weight, and temperature dependencies, chain mobility, and aging using 1-ethyl-3-methylimidazolium acetate [C2Mim][OAc], 1-butyl-3-methylimidazolium chloride [C4Mim][Cl], and 1-ethyl-3-methylimidazolium methyl-phosphonate [C2Mim][CH<sub>3</sub>(H)PO<sub>3</sub>]. Native cellulose in [C2Mim][OAc] and [C4Mim][Cl] show a yield stress when water is present but can be dried at 80 C under nitrogen for 20 minutes to revert to simple viscoelastic liquids. Contrary to previous findings, these dry solutions show only a slight decrease in intrinsic viscosity with increasing temperature when measured in a 2 RH% environment. Time-temperature-superposition (tTs) master curves of three cellulose/IL solutions were constructed to investigate the dependency of anion size on cellulose/IL association. As the anion size of IL increased ([CH<sub>3</sub>(H)PO<sub>3</sub>] > [OAc] > [Cl]), the rubbery plateau on the master curves became more enhanced. The glass transition temperatures (T<sub>g</sub>) of cellulose/IL solutions show a minimum in T<sub>g</sub> before increasing with cellulose content, indicating the perturbation of the strongly-coupled IL system by cellulose chains. For future storage purposes, the aging of cellulose in ILs is quantified through the drop of zero-shear viscosity with time, implying cellulose chain scission when solutions are stored too long at elevated temperatures.

Tuesday 2:45 Post Oak

PS22

**Rheology of linear/circular DNA mixtures in the linear entanglement regime**Dejie Kong<sup>1</sup>, Sourya Banik<sup>1</sup>, Michael J. San Francisco<sup>2</sup>, Rae M. Robertson-Anderson<sup>3</sup>, and Gregory B. McKenna<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>2</sup>*Department of Biological Sciences, Texas Tech University, Lubbock, TX 79409, United States;* <sup>3</sup>*Department of Physics and Biophysics, University of San Diego, San Diego, CA 92110, United States*

Circular polymers behave differently from the corresponding linear chains due to a topology difference induced by the constraints of no free chain ends. Compared to synthetic circular polymers, the polydispersity index of DNA is one and, potentially, a smaller amount of linear contamination can be achieved during the preparation of samples. Furthermore, the circular DNAs can, in principle, achieve the entangled regime more easily than synthetic polymers due to their large size which ranges from 10<sup>6</sup>g/mol to 10<sup>8</sup>g/mol, while the maximum size of synthetic circular polymer studied so far is 3.9x10<sup>5</sup>g/mol. The circular DNA being used for this study is a fosmid [Fos45 (45kbp)] which is produced by replication of E.Coli and then extracted. In this work, the dynamic properties of entangled circular polymers mixed with similar molecular weight linear chains are studied using rheological measurements in concentrated solution. Measurements of G'(ω) and G''(ω) as well as creep and recovery are used in the characterization of nominally entangled solutions as functions of both total DNA concentrations in solution and relative amounts of linear and circular DNA. The circular Fos45 DNA is mixed with a commercially available linear lambda phage DNA (48.5kbp) at a total solution concentration of 0.5 mg/ml, 1mg/ml, and 2 mg/ml, covering a range of entanglements from approximately 7 to 51, hence they are well entangled. By varying the amount of Fos45 added to the lambda phage DNA, we examine the effects of linear polymer on the dynamic properties of circular polymers and vice versa. Future work will examine the limiting behavior of zero percent linear chains in the circular DNAs as well as circular DNA of higher molecular weight.

Tuesday 3:45 Post Oak

PS23

**Direct observation of ring polymer dynamics in semi-dilute solutions: Coupling of molecular topology and interchain interactions**Yuecheng Zhou<sup>1</sup>, Kathryn Regan<sup>2</sup>, Dejie Kong<sup>3</sup>, Sourya Banik<sup>3</sup>, Rae M. Robertson-Anderson<sup>2</sup>, Gregory B. McKenna<sup>3</sup>, and Charles M. Schroeder<sup>4</sup><sup>1</sup>*Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Department of Physics and Biophysics, University of San Diego, San Diego, CA 92110, United States;* <sup>3</sup>*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>4</sup>*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Over the past two decades, advances in fluorescence imaging have enabled the direct observation of polymer dynamics at the single molecule level. Despite recent progress, the vast majority of studies has mainly focused on the dynamics of linear polymer chains in dilute solutions. Moving forward, there is a clear need to study the dynamics of polymers with complex molecular topologies such as ring polymers in flow. Here, we report the direct observation of ring polymer dynamics in semi-dilute unentangled solutions of linear chains in extensional flow. In particular, we characterize the transient and steady-state stretching dynamics of ring polymers in background solutions of semi-dilute linear chains across a wide range of concentrations. Remarkably, our results show that ring polymers drastically fluctuate in chain extension in extensional flow, even at so-called 'steady-state', long after the initial transient stretching process. Interestingly, such large extensional fluctuations are not observed in the steady-state stretching of linear polymers in semi-dilute solutions in extensional flows. Furthermore, even at very low concentrations of linear chains (0.025 c\*), we see large fluctuations of ring molecules in the linear background that are different from the linear chains. Based on these results, we hypothesize that ring polymer fluctuations arise due to transient threading of linear polymers through open ring polymer chains in flow. The fluctuation frequency is analyzed as a function of strain rate and background polymer concentration. Moreover, our results show that ring polymers generally exhibit markedly less molecular individualism across the molecular ensemble compared to their linear counterparts during transient stretching in extensional flow, which is attributed to circular topological constraints. Overall, this work effectively extends the study of single polymer dynamics to ring-shaped polymers in non-dilute solutions.

Tuesday 4:10 Post Oak

PS24

**Uniaxial extension of entangled polymer solutions**Jianning Liu, Yi Feng, and Shi-Qing Wang*University of Akron, Akron, OH 44325, United States*

Nonlinear response to fast uniaxial extension of entangled polymers is characterized by rubbery like elastic stretching, followed by yielding of the entanglement network before reaching a point of tensile strain localization [1]. We investigate three entangled PS solutions with low molar-mass PS as solvents as well as analogous PI solutions. We show that the nonlinear response differs among these solutions at comparable effective Hencky rates. These solutions also exhibit anomalous temperature dependence that no current theoretical understanding can provide an explanation.

[1] Nonlinear Polymer Rheology: Macroscopic phenomenology and molecular foundation, S. Q. Wang, Wiley (2018).

## Symposium DA Design of Applied Materials

Organizers: Jeffrey Martin and Matthew J. Armstrong

Tuesday 1:30 San Felipe Room

DA6

**Development of a shear-thickening fluid for use in space suits for low-Earth orbit and the lunar and Martian surfaces**Maria Katzarova<sup>1</sup>, Richard D. Dombrowski<sup>2</sup>, and Norman J. Wagner<sup>1</sup><sup>1</sup>*University of Delaware, Newark, DE, United States;* <sup>2</sup>*STF Technologies LLC, Newark, DE, United States*

The low-Earth orbit (LEO) environment exposes astronauts performing extravehicular activity (EVA) to potential threats from micrometeoroid and orbital debris (MMOD) traveling at nominal speeds of 10 km/s. STF-Armor(tm) is a nanocomposite material comprised of shear-thickening fluid (STF) intercalated into a high-strength textile. It has been shown that STF-Armor(tm) offers superior, flexible, multi-functional protection against physical hazards making them a novel candidate material component of environmental protection garments (EPGs). We have been working to improve the absorber layers of the current thermal micrometeoroid garment (TMG), soft goods portion of the EVA space suit, with STF-treated layers. The resulting STF-treated layers prevent hypervelocity impacts from piercing the life essential bladder layer of the TMG. In order to adapt STF-Armor(tm) to LEO, low-volatility hydrocarbon oils are used for the STF formulation. The aim of these investigations is the incorporation of the LEO-STF technology to improve the protection of astronaut EPGs capable of withstanding extended exposure to the space environment during multiple EVAs. LEO-STF-imbibed TMG layups will be tested for puncture, abrasion and hypervelocity impact resistance. It will be shown that a LEO-STF-treated TMG offers roughly two times greater energy dissipation than the current TMG, without sacrificing weight and thickness of the space suit. Prototype LEO-STF-containing TMG layups are currently flying on the exterior of the international space station (ISS) on the Materials ISS Experiments, MISSE-9. The samples are being exposed to extreme levels of solar- and charged-particle radiation, atomic oxygen, hard



vacuum, and temperature cycling over the course of a year. High-resolution images of the samples throughout the experiment are being collected and analyzed.

Tuesday 1:55 San Felipe Room

DA7

### **Rheology of suspension and particles interactions**

William Chèvreumont<sup>1</sup>, Hugues Bodiguel<sup>1</sup>, and Bruno Chareyre<sup>2</sup>

<sup>1</sup>LRP, CNRS, Univ. Grenoble-Alpes, Grenoble INP, Grenoble 38000, France; <sup>2</sup>3SR, CNRS, Univ. Grenoble-Alpes, Grenoble INP, Grenoble 38000, France

Suspension flows involves a wide range of phenomena which depends strongly on concentration, confinement and shear rate. Some suspensions show Newtonian behavior, but many of them also shows shear thinning and/or shear thickening. During this work, we study the influence of inter-particles interactions, and how they can modify suspension flow. End-term objective of this work is to tune the fluid properties in order to modify some phenomena like segregation, migration or clogging in a microchannel. Conventional rheometry measurement are done on suspensions of calibrated PMMA microspheres with many Newtonian fluids. Force measurement between particles are also done on those medium using an optical tweezers. Those measurements allow to determine the particles interactions, and so their microscopic behavior. The objective is to correlate these two measurements, in order to understand how the microscopic behavior can change the macroscopic one. On the other hand, suspensions are numerically simulated using a discrete element method. Simulations allows us to test a wide range of conditions and to vary some parameters that are hard to change on experiments. Secondly, simulations allows us to identify, quantify and characterize each phenomenon and its relative importance. At the end, simulation and experimental results are confronted. This allows us to validate the numerical model, and to explain the experimental phenomena. First simulations results using a minimal model composed of simple contact and friction law for solid particle interaction, and lubrication for the fluid interaction shows good agreement with experimental values and values available in literature. From this base, other inter-particles interactions, that are said to be at the origin of non-Newtonian behavior are introduced into our model.

Tuesday 2:20 San Felipe Room

DA8

### **High shear rheology of silica slurries**

Ehsan Akbari Fahkrabadi and Matthew W. Liberatore

*Chemical Engineering, University of Toledo, Toledo, OH 43606, United States*

The role of Chemical Mechanical Polishing (CMP) in semiconductor industry has become more pronounced as companies create smaller and smaller integrated circuit devices. CMP relies on the capability of producing colloidally-stable dispersions for abrasion and to transport the waste products away from the polished surface. Unstable dispersions at high polishing shear rates ( $\sim 1,000,000 \text{ s}^{-1}$ ) increase the possibility of forming particle clusters leading to surface scratching. In addition, the impact of particles shape and size on rheological behavior of slurries can determine the smoothness of the final polished surface. In the present study, the shear thickening and stability of commercially available colloidal silica slurries of two different particle sizes was tested using high shear rheology. Rheological measurements were conducted using a specialized experimental protocol uses a parallel plate geometry at 30 to 50 micron gaps, which allows for shear rates ranging from 100-200,000  $\text{s}^{-1}$ . The results collected from these processes are compared to fumed silica slurries under the same conditions. The effect of additives on slurry behavior for particle systems using salts showed the possibility of altering the thickening shear rate to lower/higher values. In addition, for spherical silica slurries with particle sizes ranging from 10 to 110 nm, an analysis of the effect of volume fraction on slurry behavior was conducted by observing the differences between the experimental data and predictions using hard sphere volume fraction-viscosity models.

Tuesday 3:45 San Felipe Room

Keynote DA9

### **Triggering microstructural changes in complex fluids: Two industry-academia partnerships**

Seth Lindberg<sup>1</sup>, Patrick Stenger<sup>1</sup>, Kelly Schultz<sup>2</sup>, Matt Wehrman<sup>2</sup>, Kendra Erk<sup>3</sup>, Carlos Martinez<sup>3</sup>, and John Howarter<sup>3</sup>

<sup>1</sup>Procter and Gamble, Cincinnati, OH, United States; <sup>2</sup>Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, United States; <sup>3</sup>Materials Engineering, Purdue University, West Lafayette, IN 47906, United States

Two collaborations between P&G & Academia for making and breaking dispersions are reviewed:

Controlling the collapse & expansion of colloidal gels upon dilution (Lehigh): Colloidal gels are commonly used to stabilize particles from settling in formulated mixtures and to impart shear-thinning behavior, which is required for dosing and consumer use. Recently, the development of naturally derived colloidal gels from cellulose and wax has broadened the use of these materials to personal, fabric and home care products. However, the evolution of particulate gels during dilution is not well studied; fibrous colloids can aggregate or collapse rather than disperse if mixed into a solvent that alters attractive forces. Understanding the changes to the microstructure upon contact with another fluid enables us to optimize industrial scale mixing and to control consumer experiences with the product (i.e., when dilution of a detergent or shampoo occurs at home).

Emulsion making and breaking (Purdue): Oily material contaminates water aboard ships, called "bilgewater". Large volumes (i.e., 3000 gallons per day) of this must be collected and cleaned ( $< 15 \text{ ppm}$  oil) prior discharging back into the ocean. Expensive onboard filtering is one solution. A less expensive formulation/process combination is desired. Purdue received a grant from the U.S. Dept. of Defense Strategic Environmental Research and Development Program (SERDP) to guide future options. This project will investigate the formation and stability of complex oil-in-water shipboard emulsions that result from on-board cleaning and mechanical operations of Armed Forces marine vessels. P&G is an industrial

sponsor which will provide expertise in surfactant science. Whereas P&G generally stabilizes emulsions of silicone or hydrocarbon oils for conditioning hair & clothes, this effort requires the de-emulsification/de-stabilization of a dispersion.

Tuesday 4:10 San Felipe Room

DA10

### **Tuning process parameters to optimize carbon nanotube fibers for high performance conductors**

Lauren W. Taylor, Oliver S. Dewey, and Matteo Pasquali

*Department of Chemical & Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Carbon nanotubes (CNTs) are well known for their outstanding electrical, mechanical, and thermal properties. However, it has proven difficult to transform these single molecule properties to macroscale materials such as fibers. Significant strides have been achieved by processing CNTs in chlorosulfonic acid. Chlorosulfonic acid and CNTs create a true solution, and the CNTs spontaneously align to form liquid crystals. This solution is extruded into a coagulation bath to form neat CNT fibers. This process is inherently complex with competing effects of mass and energy transport and the complex flow behavior of the solution. Here, we discuss some of the fundamental solution spinning parameters and how they translate to fiber properties. Some of these parameters include solution extrusion rate, CNT solution concentration, fiber draw ratio, and choice of coagulant. These parameters directly affect alignment of the CNTs, packing density of the CNTs, and morphology of the fiber. Through this process we are able to create lightweight, flexible conductors that have specific conductivity approaching copper and specific strength approaching carbon fiber. With further understanding, we aim to push the boundaries of this material further for applications such as aircraft and electrical motors.

Tuesday 4:35 San Felipe Room

DA11

### **Characterizing the weakly elastic rheological behaviors of automotive lubricants through an improved capillary breakup extensional rheometer**

Jianyi Du<sup>1</sup>, Hiroko Ohtani<sup>2</sup>, Gareth H. McKinley<sup>1</sup>, and Kevin Ellwood<sup>2</sup>

<sup>1</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;*

<sup>2</sup>*Structures & Stamping Department, Ford Motor Company, Dearborn, MI 48121, United States*

Elongational flows of complex fluids are important in a wide range of everyday phenomena such as jetting, drop impact and fragmentation. Even if the fluid is only weakly elastic, the extensional rheology of the fluid can control the final stages of the thinning process because of the large strains and singular strain rates that develop near pinch-off. Here we aim to develop an improved device to study the extensional rheology of complex fluids such as weakly-viscoelastic motor oils, paints, as well as metalworking waxes with yield stresses. In order to do so, we utilize the experimental technique of capillary thinning, and introduce an improved design of the Capillary Breakup Extensional Rheometer (CaBER) with better-controlled plate actuation and a novel environmental temperature control system. In this setup, a liquid sample is rapidly stretched by two coaxial plates, leading to a liquid bridge connecting two hemispherical liquid reservoirs at each plate. The temporal evolution of the resulting liquid bridge is controlled by inertial, viscous, elastic and capillary effects. By measuring the evolution in the mid-plane radius and the filament shape we can probe the underlying fluid properties. We first validate our setup and demonstrate this new system's capabilities using a Newtonian calibration fluid and a series of well-studied aqueous food thickeners. We then consider a number of lubricants of importance in automotive applications: first we consider two commercial synthetic 10W-30 motor oils that appear to be identically Newtonian in shear flow. Capillary thinning measurements show that these fluids can be differentiated by onset of strain-hardening close to breakup. This weakly elastic response can be understood using a second order fluid model; second we consider a commercially available waxy metalworking lubricant which exhibits a yield stress below wax appearance temperature (of 47°C) altering the filament profiles, but then behaves as a simple Newtonian liquid even at high strain rates close to breakup.

## **Symposium BA Biological and Active Matters**

Organizers: Pushkar Lele and Kelly Schulz

Tuesday 1:30 Tanglewood

BA19

### **Propulsion of catalytic Janus spheres in viscosified solutions**

Patrick T. Underhill, Purba Chatterjee, and Edmund M. Tang

*Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

The influence of the swimming medium on propulsion at low Reynolds number has been observed for a large number of swimming microorganisms. Beyond the biological realm, studies on low-Re motion of artificial swimmers have also been carried out. For example, the use of Janus particles to make active motors has received much attention. Many applications of such motors involve moving objects through complex environments that are mixtures of components. The flow properties of these mixtures could be Newtonian or non-Newtonian. In other applications, additives may be introduced as a way of controlling the motion of motors. The first step in understanding how the fluid mixtures alter their motion is to examine propulsion in fluids where additives change the shear viscosity while the fluid remains Newtonian. We show how solution viscosity affects Janus motor propulsion keeping all other factors (motor size, fuel concentration, temperature, etc.) constant. The velocity is shown to decay approximately inversely with viscosity. Further, the type of viscosifier used affects the interaction between fuel molecules and motor, which affects propulsion. This is part of the overall goal of understanding how solution properties impact propulsion independent of a particular

application. When qualifying the propulsion in crowded environments, it is important to understand how to accurately quantify the response. We have used computer simulations to quantify the errors associated with particle tracking when extracting the propulsion of Janus motors.

Tuesday 1:55 Tanglewood

BA20

### **Mixing of active suspensions in chaotic flow**

Brendan C. Blackwell, Boyang Qin, and Paulo E. Arratia

*Mechanical Engineering & Applied Mechanics, University of Pennsylvania, Philadelphia, PA, United States*

In this talk, we examine the effect of swimming bacteria on transport, diffusion, and mixing in weakly chaotic flows. An oscillatory two-dimensional flow is generated by driving a sinusoidal current through a conducting fluid (salt water) that is situated atop an array of magnets. We perform experiments with two different arrangements of the magnets: one that is a neatly ordered lattice to create regular vortices, and on that is random to create a more disordered flow pattern. By changing the frequency and amplitude of the applied voltage we are able to probe Reynolds numbers ranging approximately from 1 to 100, and path lengths of approximately 0.1 to 1, which is sufficient to observe the onset of time-reversal asymmetry. Two types of fluids are used: (1) a simple Newtonian liquid (i.e. water) and (2) a mixture of water and bacteria (*Vibrio cholerae*). The fluids are seeded with fluorescent particles, and particle-tracking software is used to quantify the flow. Measurements of stretching fields and Lyapunov exponents are used to characterize flow behavior and mixing. Results with plain salt water are compared to results with the addition of varying concentrations of *V. cholerae*. We find that the addition of active bacteria, even in dilute quantities, results in significant changes to the stretching fields even though the Eulerian velocity fields remain quite similar. We also perform experiments with fluorescent dye, both with and without bacteria, to more directly characterize mixing. These data also show a substantial difference between the active suspension and the control case, even with small concentrations of bacteria.

Tuesday 2:20 Tanglewood

BA21

### **Silk: A natural example of a sticky entangled polymer**

Charley Schaefer<sup>1</sup>, Peter R. Laity<sup>2</sup>, Christopher Holland<sup>2</sup>, and Thomas C. McLeish<sup>1</sup>

<sup>1</sup>*University of York, York, United Kingdom*; <sup>2</sup>*The University of Sheffield, Sheffield, United Kingdom*

The mechanical properties of polymers can be greatly enhanced using a small fraction (<10%) of sticky monomers, such as ionic or dipolar groups. In the (soft) condensed state, these groups self-organise to form a dynamic network with rubber-like properties. The properties are determined by the chemistry of the sticky monomers and their distribution over the backbone of a polymer chain. While it remains greatly challenging to control the regularity of the sticker distribution and the polydispersity of the synthetic polymer, excellent control may be achieved in a natural way: We show that the linear viscoelasticity of the (semi-dilute) silk protein in the gland of the *Bombyx mori* silk worm is excellently described by linear viscoelasticity models. However, natural variations of the ion concentrations as well as temperature variations point at important shortcomings of the state-of-the-art sticky-reptation models.

Tuesday 2:45 Tanglewood

BA22

### **Fully-resolved simulation of undulatory swimming of *C. elegans* in viscoelastic fluids via the immersed boundary technique**

Christopher Guido, Jeremy Binagia, and Eric S.G. Shaqfeh

*Chemical Engineering, Stanford University, Stanford, CA 94305, United States*

The swimming behavior of microorganisms in viscoelastic fluids is of great interest since their natural fluid environments often have a rich microstructure comprised of large polymeric biological molecules. The undulating swimmer *C. Elegans* is an excellent case study since it is both experimentally well-studied and the microorganism's motion resembles the behavior of many other biological structures, like cilia or flagella. Additionally, there is a well-known speed decrease as the Deborah number increases that has been experimentally observed but, to date, has not been studied numerically with a fully resolved three-dimensional simulation. In this talk, we discuss the computer simulation of the arbitrary motion of an undulating swimmer that occupies finite volume in three dimensions including the ability to specify a viscoelastic model of our choosing in the fluid. In the present application, we discuss a modified version of the Immersed Finite Element Method (IFEM) presented by Zhang et al. (2007) that allows for the simulation of deformable swimmers in viscoelastic flows with an added conformation-driven force that allows the swimmer to evolve through an arbitrary set of specified shapes. This simulation tool is validated against experimental speed data provided by Shen and Arratia (2011) and the speed reduction as a function of Deborah number is presented with good agreement for Oldroyd-B fluids. The tool is then further used to explore the underlying physical mechanism that drives swimming speed reduction in viscoelastic fluids, including comparison to other more simplified simulations/theories. It is found that the full three-dimensional deformation gradient in the volume occupied by the solid swimmer contributes to the swimming speed and trajectory, a feature not included in lower order line-element models. The simulation tool also has the capability to simulate multiple swimmers and more complex swimming geometries opening many new possibilities for future studies of swimmers in viscoelastic fluids.

## Symposium FE Foams, Emulsions & Interfacial Rheology

Organizers: John Frostad and Joseph Samaniuk

Tuesday 3:45 Tanglewood

FE1

### **Confined bubble flow through suspensions of surface active particle–surfactant complexes**

Charles C. Sharkey, Zixian Cui, and Shelley Anna

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

Bubbles flowing through the confined geometry of a fluid filled capillary tube are affected by the presence of surface active molecules or particles that modify the interfacial mechanics. Molecular surfactants adsorb to the bubble interface and lead to Marangoni stresses that result in changes to the bubble shape as the capillary number and bubble length vary. Surface active particles also lead to Marangoni stresses, but additionally impart significant interfacial elasticity. We investigate the case of bubble flow in a capillary filled with surface active particle surfactant complexes. Silica nanoparticles are coated with cetyltrimethylammonium bromide (CTAB) in a glycerol water suspension to form the surface active complexes. Bubbles are dispensed via a co-flow capillary apparatus and the initial bubble length is varied. Capillary number is varied by adjusting the bubble velocity and suspension viscosity through the glycerol concentration. Fluid film thickness is measured along the length of the bubble at different positions in the capillary. These measurements are compared to bubble flow through surfactant solutions and to predictions from a Bretherton-type model. Two critical bubble lengths are observed. Above the first critical length, two fluid film regions are observed: a thin film and a thickened film. Bubbles flowing through suspensions of particle surfactant complexes behave similar to those flowing through surfactant solutions. Above the second critical length, the bubble tail cap begins to collapse. The results provide insight into mechanisms and processes to coat bubbles with particles in a controlled way for the production of elastic capsules.

Tuesday 4:10 Tanglewood

FE2

### **Role of interfacially adsorbed particles in the rheology of solid-stabilized emulsions**

Max Kaganyuk and Ali Mohraz

*UC Irvine, Irvine, CA, United States*

Pickering emulsions rely on solid particles to stabilize fluid-fluid interfaces and are commonly found in many applications including pharmaceuticals, petroleum refining and consumer products. Depending on their preparation and physicochemical conditions, these multiphase mixtures can exhibit rich viscoelasticity along the entire liquid-like to solid-like spectrum, which can be quite different from their surfactant-stabilized counterparts. The purpose of this study is to investigate how the presence of interfacially adsorbed particles, as opposed to surfactants, influences the microstructure and rheology of Pickering emulsions. We use a mixed aqueous/organic fluid system with refractive indexes similar to those of the colloidal particles. These systems allow us to investigate the mixture's microstructure in 3D and rheology by quantitative confocal microscopy, coupled with standard rheological measurements. We examine in detail how the excluded volume of the solid particles, their ability to be shared between two different fluid interfaces and induce droplet bridging, and interparticle interactions both along and across droplet interfaces, influence the viscoelasticity of solid-stabilized emulsions all the way from dilute systems to high internal phase emulsions. We will show how droplet bridging can significantly enhance the mixture's elasticity, and discuss similarities between this class of Pickering emulsions and colloidal gels. Finally, the role of capillary interparticle interactions and interfacial elasticity in mediating droplet coalescence and bridging, and the resultant rheology in high internal phase emulsions will be discussed. Our findings have important implications for a wide range of industries that utilize multiphase mixtures of fine particles and immiscible fluids to create new food formulations, cosmetic products, and composite materials.

Tuesday 4:35 Tanglewood

FE3

### **Engineering the mechanical properties of oil-water interfaces using nanoparticle surfactants**

Anju Toor<sup>1</sup>, Joe Forth<sup>1</sup>, Simone Bochner de Araujo<sup>2</sup>, Maria Consiglia Merola<sup>3</sup>, Yufeng Jiang<sup>1</sup>, Yu Chai<sup>1</sup>, Paul D. Ashby<sup>1</sup>, Gerald G. Fuller<sup>2</sup>, and Thomas Russell<sup>1</sup>

<sup>1</sup>*Lawrence Berkeley National Laboratory, Berkeley, CA, United States*; <sup>2</sup>*Department of Chemical Engineering, Stanford University, Stanford, CA, United States*; <sup>3</sup>*Alcimed, Lyon, France*

Nanoparticle surfactants are formed at liquid-liquid interfaces due to the adsorption of both functionalized nanoparticles dispersed in an aqueous phase and polymeric surfactant dispersed in an oil phase. The irreversible adsorption of nanoparticles to oil-water interfaces can be used to shape liquids into complex shapes. Understanding and controlling the mechanical properties of the nanoparticle surfactants provides a unique opportunity to produce novel, dimensionally confined materials at the interface between the fluids, while simultaneously generating a new class of architected, all-liquid systems. In this work, we demonstrate the ability to vary the mechanical properties of complex oil-water interfaces by orders of magnitude by tuning the interactions between nanoparticle surfactants. Continuum mechanical relations between the bending and shear moduli break down for the nanoparticle films. The shear modulus of the nanoparticle surfactant assembly is primarily governed by particle-particle interactions, while the bending modulus is determined by steric interactions between polymers that are bound to the nanoparticles. The method by which our nanoparticle films are assembled at the oil-water interface is highly versatile, and compatible with a broad range of nanoparticles with numerous properties (plasmonic, magnetic, catalytic). Our work paves the way for the development of designer, multi-component oil-water interfaces with well-defined mechanical, structural, and functional properties.

Tuesday 5:00 Tanglewood

FE4

**Dual color Bessel beam microscopy to measure absolute three phase contact angle of microparticles**Anisul Islam, Gordon F. Christopher, and Craig Snoeyink*Texas Tech Univ, Lubbock, TX 79423, United States*

The properties of Pickering Emulsions or particle stabilized droplets are highly dependent upon the three-phase contact angle of the particles which is not a monolithic value for the population of interfacial particles. A better understanding of how the distribution of contact angles varies in response to surface coverage, particle-particle interactions, and even particle shape will improve our understanding of the physical behavior of these interfaces. We will present a new method for measuring the absolute three-phase contact angles of statistically robust populations of interfacial particles. This method uses dual-color Bessel Beam Microscopy to localize both fluorescent micro- and nanoparticles in three dimensions to determine both the location of the interface and the contact angle of particles adsorbed to it. This method is capable of observing even very dense surface overages and determining both the mean contact angle and orientation of ellipsoidal interfacial particles.

**Symposium NF****Non-Newtonian Fluid Mechanics & Flow Instabilities**

Organizers: Aditya Khair and Christian Clasen

Tuesday 1:30 Plaza II

NF6

**Consequences of the mobility of particles in viscoelastic shear flow**Eric S.G. Shaqfeh, Anni Zhang, William L. Murch, and Einarsson Jonas*Chemical Engineering, Stanford, Stanford, CA 94305, United States*

We perform direct numerical simulations of single particle mobility in the vorticity, gradient, and flow direction of simple shear flow in a viscoelastic fluid at low and finite particle Reynolds number. We demonstrate that our results match closely to previous theoretical work by Einarsson & Mehlig (2017) in the limit of low shear Weissenberg number ( $Wi$ ) and low particle Deborah Number ( $De$ ). For particle motion created by a force  $F$  in the shear flow direction, we find that the particle will tend to drift in the  $F \times \Omega$  direction, where  $\Omega$  is the flow vorticity, at all values of the  $Wi$  and  $De$  examined. This implies, for example, that a sedimenting particle suspension can become unstable due to concentration fluctuations (as first suggested by Vishnampet & Saintillan, 2012). We then present experimental evidence that demonstrates this effect. Moreover, motion in the  $F \times \Omega$  direction is the opposite of that observed due to inertial forces in Newtonian fluids - commonly termed "Saffman lift" (Saffman, 1965). Recent observations in microfluidic devices demonstrate this effect. Thus, we perform new particle resistance simulations at both small and finite Reynolds Number ( $Re$ ) to predict at which point elastic and inertial forces balance and the lift force changes sign. Finally, if time permits, the consequences of these results on convective-diffusion (i.e. Taylor dispersion) of particles in viscoelastic shear flow will be discussed.

Tuesday 1:55 Plaza II

NF7

**Dynamics and rheology of particles in shear-thinning fluids**Charu Datt, S. Arman Abtahi, and Gwynn J. Elfring*Department of Mechanical Engineering, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada*

The dynamics of particles in non-Newtonian fluids can be markedly different than in Newtonian fluids. In this talk, we present analytical results for the motion of spheres and spheroids in weakly shear-thinning fluids. We also discuss how the motion of active particles is non-trivially affected by the shear-thinning rheology. The results are obtained using the reciprocal theorem of low Reynolds number hydrodynamics which we also use to calculate the first correction to the suspension viscosity, the Einstein viscosity, for a dilute suspension of spheres in a weakly shear-thinning fluid.

Tuesday 2:20 Plaza II

NF8

**Viscoelastic ordering of particles in a straight microfluidic channel**Francesco Del Giudice<sup>1</sup>, Gaetano D'Avino<sup>2</sup>, Francesco Greco<sup>2</sup>, Amy Q. Shen<sup>3</sup>, and Pier Luca Maffettone<sup>2</sup>*<sup>1</sup>Systems and Process Engineering Centre, College of Engineering, Swansea University, Swansea, United Kingdom; <sup>2</sup>Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, Università degli Studi di Napoli Federico II, Napoli, Italy; <sup>3</sup>Okinawa Institute of Science and Technology Graduate Univers, Okinawa 904-0495, Japan*

Microfluidics, i.e., systems made by fluids flowing in channels with micron length scale, has received a growing interest in engineering, biology, and medicine. In numerous applications, biological or man-made microparticles are suspended in fluids for counting, sorting, analysis, and detection. In these applications, the manipulation of particle trajectories is crucial. Recent studies have shown that viscoelastic suspending fluids can be used to efficiently align the flowing particles on the channel centerline (3D focusing). In many applications, however, it is also desired that the aligned particles self-assemble in equally-spaced structures. This particle ordering is, for instance, required in encapsulation of particles in droplets where the frequency of droplet formation must be synchronized with the frequency of particles entering the encapsulation area. In this contribution, we show by experiments and numerical simulations that, once 3D focusing is achieved, fluid viscoelasticity can lead to the formation of equally-spaced particle structures. We employ an elastic, shear-thinning hyaluronic acid solution in phosphate buffer saline (PBS). We find that particles of 20  $\mu\text{m}$  in diameter flowing at 100  $\mu\text{l}/\text{min}$  in a straight square-shaped microchannel with height of 100  $\mu\text{m}$  can be equally spaced with

a high efficiency. Simulations are carried out for a train of particles aligned along the channel centerline by solving the particle motion equations where the particle velocities are taken from direct numerical simulations on a three-particle system. The spacing efficiency is evaluated by varying the particle concentration, the fluid rheology, and the flow rate. A good quantitative agreement between experiments and simulations is found.

Tuesday 2:45 Plaza II

NF9

### **Steady viscoelastic flow around high-aspect-ratio, low-blockage-ratio microfluidic cylinders**

Simon J. Haward, Kazumi Toda-Peters, and [Amy Q. Shen](#)

*Okinawa Institute of Science and Technology Graduate Univers, Okinawa 904-0495, Japan*

We employ a state-of-the-art microfabrication technique to produce microfluidic cylinder geometries that explore new geometrical regimes. Two microchannels are fabricated in monolithic fused silica substrate with height  $H = 2$  mm and width  $W = 0.4$  mm (aspect ratio  $a = H/W = 5$ ) containing cylinders of radius  $r = 0.02$  mm (blockage ratio  $\beta = 2r/W = 0.1$ ), centered at the channel mid-width,  $W/2$ . An 'sc' channel contains a single cylinder, while a 'dc' channel contains two axially aligned cylinders separated by a distance  $L = 1$  mm ( $L = 50r$ ). These rigid glass devices provide a quasi-two-dimensional flow along the direction of the cylinder axis and also more clearly reveal the effects of the strong extensional wake regions located at the leading and trailing stagnation points. Using flow velocimetry and quantitative birefringence measurement techniques, we study the behavior of a well-characterized viscoelastic polymer solution in flow around the cylinders. The small cylinder radii result in low inertia and very high elasticity numbers  $Ei \sim 2400$ . For the sc device, we report strong flow modification effects around the cylinder as the flow rate is incremented. This is associated with the deformation of polymer molecules primarily in the upstream wake region, leading to the onset of a purely elastic flow asymmetry upstream of the cylinder. Stretched polymer molecules are advected around the cylinder and relax downstream of the cylinder, resulting in an extremely long elastic wake extending for  $>300r$  downstream. In the dc channel, at lower flow rates, similar flow modification effects are observed to develop around, and downstream of, both cylinders. However, at higher flow rates the wake of the first cylinder extends  $>50r$  downstream, and begins to interact with the second cylinder. The second cylinder becomes encapsulated by the wake of the first and is effectively obviated from the flow field. The results are useful for benchmarking against numerical simulations using viscoelastic constitutive models.

Tuesday 3:45 Plaza II

NF10

### **Elasto-inertial turbulence: Reentrant transition and connection to linear mechanisms**

[Ashwin Shekar](#)<sup>1</sup>, Ryan McMullen<sup>2</sup>, Sung-Ning Wang<sup>1</sup>, Beverley McKeon<sup>2</sup>, and Michael D. Graham<sup>1</sup>

<sup>1</sup>*Chemical and Biological engineering, University of Wisconsin-Madison, Madison, WI, United States;* <sup>2</sup>*Engineering and Applied Science, Caltech, Pasadena, CA, United States*

We describe direct numerical simulations (DNS) of channel flow turbulence in a FENE-P fluid. At Reynolds numbers very close to transition, the flow first relaminarizes upon increasing Weissenberg number ( $Wi$ ) or polymer concentration, but then becomes turbulent again, displaying features of elasto-inertial turbulence (EIT). At higher Reynolds number, the flow evolves as  $Wi$  increases from displaying intermittency and streamwise vortex structure characteristic of Newtonian flow to EIT, while at intermediate  $Wi$ , a spatiotemporal mixture of the two structures is observed. We tie these observations to the 2D stability of the laminar flow and characterize the observed disturbance amplification which starts to show up at intermediate  $Wi$ . Observations point at a bypass transition which bears strong resemblance to a discrete eigenmode close to the real axis in the eigenvalue spectrum. Further, we present a tentative bifurcation scenario associated with this mode and draw links to Tollmien-Schlichting modes in the Newtonian limit and Gorodtsov-Leonov modes in the elastic limit.

Tuesday 4:10 Plaza II

NF11

### **Vortex dynamics for high levels of polymer drag reduction: Quantitative analysis enabled by a new vortex-tracking algorithm**

[Lu Zhu](#) and Li Xi

*Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada*

Drag reduction caused by flexible polymers in wall-bounded turbulence has been studied for decades. A small dosage of polymers will significantly change flow structures in turbulence, and further reduce the energy losses due to the friction drag. Understanding the drag reduction phenomenon has significant practical implications for developing advanced flow control schemes. Turbulent dynamics undergo several stages of transitions as the fluid elasticity induced by drag-reducing polymeric additives increases. In particular, previous experimental and numerical studies have shown that flow statistics become qualitatively changed once the high-extent drag reduction (HDR) regime is reached, suggesting the onset of a new drag reduction mechanism. In our current study, this mechanism is explained from the aspect of vortex dynamics. A new method for vortex tracking, termed vortex axis tracking by iterative propagation (VATIP), is developed to identify and extract three-dimensional vortices from the complex turbulent background. The method enables the quantitative and statistical analysis of the distribution and configuration of generic vortices, including highly curved ones such as hairpins. A new procedure is also proposed for the classification of vortices based on their axis topologies. Application of these new methods to viscoelastic turbulent flow fields reveals a new mechanism for the changing vortex dynamics during the transition towards HDR. Polymers in the HDR regime tend to suppress the bursting phenomenon of turbulence by preventing the lifting process of near-wall vortices. This effectively suppresses vortex regeneration from the streak-instability mechanism and exposes the parent-offspring mechanism as the primary pathway for turbulence sustenance. The drastic change of the vortex regeneration mechanism qualitatively modifies the formation and distribution of vortices in the flow field and hence is responsible for the localization of turbulent structures and for the unique flow statistics observed at HDR.

Tuesday 4:35 Plaza II

NF12

### **Common features between the Newtonian transition to turbulence and the viscoelastic drag reducing turbulence**

Anselmo S. Pereira<sup>1</sup>, Roney L. Thompson<sup>2</sup>, and Gilmar Mompean<sup>3</sup>

<sup>1</sup>*Centre de mise en forme des matériaux, MINES ParisTech, Nice CS 10207, France;* <sup>2</sup>*Mechanical Engineering, UFRJ, Rio de Janeiro, Brazil;* <sup>3</sup>*Mechanical Engineering, Université de Lille, Lille, France*

Transition from laminar to turbulent flows still challenges the scientific community since the seminal work of O. Reynolds. Recently, experimental and numerical investigations on this matter have demonstrated that the spatio-temporal dynamics associated to transitional flows belongs to the directed percolation class. In the same grounds, simulation of predator-prey models, the meso-scale turbulence in fluidized biological systems, and the analogy of the localized excitation in the membrane potential that propagates along the nerve axon also corroborate in many aspects the universality that characterizes the transitional flows. Here, we explore a new perspective of this universality by examining laminar-turbulent transition from the viewpoint of the recent theoretical development that concerns viscoelastic turbulence, i.e. the drag reducing turbulent flow obtained from adding polymers onto a Newtonian fluid. We found remarkable fingerprints of the variety of states that are present in both types of flows, as captured by a series of features that are known to be present in drag reducing viscoelastic turbulence. In particular, when compared to a Newtonian fully turbulent flow, the universal nature of these flows includes: i) the statistical dynamics of the alternation between active and hibernating turbulence; ii) the decay of elliptical and hyperbolic structures, iii) the existence of a high (HDR) and a low drag reduction (LDR) subregimes with the same boundary; iv) the relative enhancement of the streamwise normal stress; and v) the slope for the energy spectrum decay with respect to the wave number.

Tuesday 5:00 Plaza II

NF13

### **Plant sourced biopolymers for turbulent drag reduction**

Anoop Rajappan and Gareth H. McKinley

*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

The cost of polymer additives has been a key impediment in the adoption of polymer drag reduction techniques in large-scale marine applications. In this study, we investigate the mucilage extracted from the bran of plant seeds such as flax, chia and psyllium, as potential sources of inexpensive, water-soluble, high molecular weight polymers for drag reduction in turbulent boundary layer flows. To this end, skin friction measurements in dilute solutions of both synthetic as well as plant-based high polymers are performed using a custom-built Taylor-Couette apparatus, operating in the fully turbulent flow regime, at Reynolds numbers between 11000 and 86000. As a specific example, we characterize the drag reducing properties of the aqueous mucilage extracted from flax seeds (*Linum usitatissimum*), and compare its performance to that of a commonly used synthetic polymer, namely, polyethylene oxide (PEO). The molecular and viscoelastic properties of the principal polysaccharide constituent in flax mucilage is also studied using size exclusion chromatography and extensional rheology techniques (CaBER). Finally, we compare the shear-induced degradation of both polymers under prolonged turbulent flow conditions, and explore the possibility of mitigating chain-scission processes by the use of surfactant additives. The dilute mucilage solutions are seen to exhibit comparable drag reduction and degradation behavior as aqueous PEO, and can possibly serve as an effective, eco-friendly, and economical alternative to synthetic polymers in real-life drag reduction applications.





## Wednesday Morning

### Symposium PL Plenary Lectures

Wednesday 8:30 Galleria I

PL3

#### **Connecting rheology to nanoscale structure of block copolymer micelle liquid crystals and nanocomposites**

Lynn M. Walker

*Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, United States*

At high polymer concentrations, solvent-selective block copolymer molecules self-assemble into concentrated micellar solutions that form highly-ordered, nanostructured, soft solids. Controlling the solvent quality allows for high densities of deformable (soft) particles to be achieved. Solvent stable nanoparticles dispersed in these soft solids will sample the solvent-swollen continuous structure providing a method to template, store, and define the environment of nanoparticulate material. Dispersed phase materials including metal oxide nanoparticles and globular proteins have been studied, providing composite systems in two interesting limits; hard particles dispersed in a dense dispersion of soft particles and a dense dispersion of soft particles with a bimodal level of softness. We characterize the impact of added nanoparticles on the local micelle packing, flow mechanism, and overall structure of the soft solid. These materials have rich phase behavior offering considerable potential in templating, transport properties and nanostructure control through both molecular design and processing.

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Wednesday 9:50 Galleria I

Keynote SC27

#### **Industrial suspension rheology as a tool to solve complex engineering problems**

Babak Derakhshandeh

*Strategic Technology Development, Suncor Energy Inc, Calgary, Alberta T2P 3E3, Canada*

Knowledge of the flow behaviour of suspensions has long been of significant importance for a wide range of industries for proper design of unit operations, for efficient transport of the products, and for proper management of waste by-products. Canadian oil sands is one of the largest industries dealing with processing of colloidal suspensions during hydro-transport, flotation, bitumen froth processing, and fluid tailings treatment. In this presentation, some of the past research activities focused on understanding of the rheology of suspensions in the oil sands will be reviewed. The presentation will be delivered in two parts. In part I, the main attributes and constraints of industrial research will be reviewed. In part II, three examples of past research on rheology of industrial suspensions will be discussed. First study includes understanding the rheology of oil sands fluid tailings. The difficulties in measuring the rheology of these suspensions will be discussed and their rheology will be compared with that of a kaolinite suspension prepared at the same particle size distribution and zeta potential. The second study will focus on the development of an "approximate" methodology to measure rheology of a non-homogenous, self-lubricating suspension with the ultimate goal of developing pipeline pressure drop correlations for designing a commercial scale transport line. It will be shown how a complex non-Newtonian flow problem was simplified to provide process engineering information within a limited timeline using the concepts of conventional rheometry. The third topic will focus on flow of bubbles in yield stress fluids. A complex non-Newtonian flow problem is simplified to various steps in order to provide knowledge on how bubbles flow in a yield stress fluid of various rheological and morphological characteristics. The percolation threshold and the gas release mechanisms from the yield stress fluids will also be discussed based on the experiments conducted on model and real fluids in the laboratory.

Wednesday 10:15 Galleria I

SC28

#### **Impact of polymer binder molecular weight on battery slurry rheology and electrochemical performance**

Samantha L. Morelly, Maureen H. Tang, and Nicolas J. Alvarez

*Chemical Engineering, Drexel University, Philadelphia, PA 19104, United States*

Battery electrodes are composed of active and inactive materials. The inactive materials fall into two categories: conductive additive and polymer binder. The active material is the ion source within in the battery, while the conductive additive ensures sufficient electron transport. The polymer binder is used to increase the mechanical stability of the electrode and its adhesion to the current collector. Previous work by our group investigated the role of conductive additive in battery slurries and found that nanosized carbon black creates a colloidal gel at critical volumes fractions ( $f = 0.02$ ) independent of the presence of micron sized Non-Brownian active material particles. We found that the slurry rheology is strongly dependent on whether carbon is free in solution or bound to the active material surface, which can be correlated to the electrode performance. Several studies have alluded to a correlation between slurry microstructure and battery performance. While in our previous studies we controlled the slurry microstructure via conductive additive, we now determine the effect of polymer molecular weight (Mw) on slurry microstructure with constant free conductive additive to further test this concept. In battery slurries the polymer binder creates a depletion force on colloidal particles that is

proportional to concentration and Mw of the polymer. In practical cases, higher Mw of polymer is preferred in order to maximize electrode mechanical properties, but results in a lower interaction potential between colloidal particles and thus a vastly different slurry microstructure. This work investigates the impact of polymer Mw on the colloidal behavior of battery slurries and whether there exists a correlation to the electrochemical performance of the final electrode.

Wednesday 10:40 Galleria I

SC29

### **Rheological investigation of fuel cell catalyst inks**

Sunilkumar Khandavalli<sup>1</sup>, Jae H. Park<sup>2</sup>, Nancy N. Kariuki<sup>2</sup>, Deborah J. Myers<sup>2</sup>, Jonathan J. Stickel<sup>3</sup>, Katherine Hurst<sup>1</sup>, K.C. Neyerlin<sup>1</sup>, Michael Ulsh<sup>1</sup>, and Scott A. Mauger<sup>1</sup>

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Proton exchange membrane fuel cells are one of the promising energy technologies due to their clean energy emissions, high energy conversion efficiency for many applications as portable or stationary power sources and automobiles. The catalyst layer forms a critical component of fuel cells, where the electrochemical reactions occur. It is commonly fabricated from a catalyst ink formulation using various deposition methods. The microstructure of the ink formulation and how it is processed during the fabrication, strongly impacts the final catalyst layer morphology and electro-chemical performance. A rheological study was conducted on the inks to investigate the underlying interactions between ink components and the impact on bulk microstructure. The ink consists of platinum (Pt) nanoparticles supported on carbon black and ionomer dispersed in an organic/aqueous solvent. The effects of carbon surface area, Pt loading and ionomer content on the rheology of inks was studied in combination with ultra-small angle x-ray scattering experiments. The addition of Pt caused a decrease in viscosity of both carbons due to electrostatic stabilization of the aggregates. For Pt-free carbons, the addition of ionomer predominantly resulted in a decrease in the viscosity associated with electro-steric stabilization of the carbon aggregates. Whereas in the case of Pt-loaded carbons, the addition of ionomer demonstrated interesting differences in the rheological behaviors between the two carbons. In a low surface area carbon the ionomer was found to stabilize the carbon aggregates causing a decrease in the viscosity. Whereas in a high surface area carbon, the ionomer appeared to flocculate the carbon aggregates resulting in an increase in the viscosity. We attribute the differences in the rheological behavior between the two Pt-loaded carbons to strong variations in the ionomer coverage associated with their different Pt distribution, that likely modified the inter-particle interactions.

Wednesday 11:05 Galleria I

SC30

### **Rheological properties of corn stover slurries during fermentation by *Clostridium thermocellum***

Sanchari Ghosh, Evert K. Holwerda, Robert S. Worthen, Lee R. Lynd, and Brenden P. Epps

*Thayer School of Engineering, Dartmouth College, Hanover, NH 03755, United States*

A novel process called “cotreatment” (consolidated bioprocessing with intermittent milling) has recently been proposed for biological conversion of lignocellulose to biofuels. Corn stover is of particular interest as feedstock to produce ethanol. In order to inform the feasibility of cotreatment, the material properties of corn stover during fermentation need to be characterized. We have characterized the rheology of small-particle, corn stover slurries undergoing fermentation by *Clostridium thermocellum* by performing flow sweep tests and large amplitude oscillatory shear (LAOS) experiments. All tested concentrations of corn stover slurries were found to be shear-thinning and well described by a power law model, with a power law exponent of 0.10. Plastic viscosities ranged between 2000 to 1 Pa.s, depending on the solids concentration and extent of conversion. Upon fermentation, plastic viscosity rapidly decreased by a factor of 2000, with the first 8-fold reduction occurring in the first 10% solubilization (out of 61% total solubilization). LAOS experiments revealed only minor changes to the rheological fingerprint of the slurry, the notable change being a reduction in the critical strain amplitude needed for the onset of nonlinearity. Both unfermented and partially-fermented slurries were found to be elastoviscoplastic, with the elastic/viscous crossover at roughly 100% strain amplitude. This talk presents new and exciting results that have favorable but not definitive implications for the feasibility of cotreatment.

Wednesday 11:30 Galleria I

SC31

### **Shear-induced microstructural evolution and implications for the rheo-dielectric behavior of carbon black suspensions**

Julie B. Hipp<sup>1</sup>, Jeffrey J. Richards<sup>2</sup>, and Norman J. Wagner<sup>1</sup>

<sup>1</sup>*University of Delaware, Newark, DE, United States;* <sup>2</sup>*NCNR, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

The shear-induced behavior of carbon black suspensions is highly relevant due to the widespread use of these materials in applications where flow is an important aspect of processing and end use. In these applications, macroscopic properties such as the viscosity and electrical conductivity of the suspension are key design parameters that are ultimately determined by the suspension microstructure. While much research has been aimed at understanding the relationship between the microstructural and macroscopic properties of carbon black dispersed in a variety of media including oils, polymers, and alkyl carbonates, a direct measurement of the structure of these suspensions while under shear has been challenging. In this work, a Rheo-USANS (Ultra-Small Angle Neutron Scattering) instrument is used to measure the shear-induced microstructure and resulting macroscopic rheological response of a commercially available conductive carbon black, Vulcan XC-72, suspended in Newtonian fluids. The shear-induced dielectric properties of these suspensions are measured and directly related to the observed microstructural evolution from Rheo-USANS measurements. These experiments confirm that the shear-thinning behavior commonly observed in these suspensions arises due to the erosion of

carbon black agglomerates with increasing shear rate. The effect of shear is also observed in the electrical properties where upon yielding, a system-spanning network of inter-agglomerate bonds is broken and a consequent decrease in electrical conductivity is observed. With increasing shear rate, however, the observed structural erosion gives rise to different trends in conductivity depending on the suspending medium. Both the rheological and electrical consequences of the flow-induced microstructure of this suspension have implications for the design and improvement of many technologies including energy storage devices, inks, and polymer composites.

## Symposium PM Polymer Melts: From Molecular Rheology to Processing

Organizers: Reza Foudazi and Richard Graham

Wednesday 9:50 Plaza I

PM14

### Chain length dispersity effects on viscoelastic response of entangled polymers

Gary S. Grest<sup>1</sup>, Brandon L. Peters<sup>1</sup>, K. Michael Salerno<sup>2</sup>, Ting Ge<sup>3</sup>, and Dvora Perahia<sup>4</sup>

<sup>1</sup>Sandia National Laboratories, Albuquerque, NM 87185, United States; <sup>2</sup>U.S. Army Research Laboratory, Aberdeen, MD, United States; <sup>3</sup>Mechanical Engineering and Materials Science, Duke University, Durham, NC 27710, United States; <sup>4</sup>Department of Chemistry, Clemson University, Clemson, SC, United States

While essentially all theoretical and computational studies of entangled polymer melts have focused on uniform samples, polymer synthesis routes always result in some dispersity, albeit narrow, of distribution of molecular weights ( $\bar{M}_w/\bar{M}_n \sim 1.02-1.04$ ). Here the effects of dispersity on chain mobility and viscoelastic response are studied for entangled, disperse melts using a coarse-grained model for polyethylene. Polymer melts with chain lengths set to follow a Schulz-Zimm distribution for the same average  $M_w = 36$  kg/mol with  $\bar{M}_w = 1.0$  to 1.16, were studied for times of 600 - 800  $\mu$ s using molecular dynamics simulations. This time frame is longer than the time required to reach the diffusive regime. We find that dispersity in this range does not affect the entanglement time or tube diameter. However, while there is negligible difference in the average mobility of chains for the uniform distribution  $\bar{M}_w = 1.0$  and 1.02, the shortest chains move significantly faster than the longest ones offering a constraint release pathway for the melts for larger  $\bar{M}_w$ . The stress autocorrelation function was fit to the theoretical expression proposed by Likhtman and McLeish. The resulting plateau modulus, terminal time and viscosity all decrease with increasing dispersity, corresponding to an apparent increase in the entanglement molecular weight.

Wednesday 10:15 Plaza I

PM15

### Effects of branching on rheology of polyethylene combs: A molecular dynamics simulation study

Dvora Perahia<sup>1</sup>, Sidath Wijesinghe<sup>1</sup>, and Gary S. Grest<sup>2</sup>

<sup>1</sup>Department of Chemistry, Clemson University, Clemson, SC 29634, United States; <sup>2</sup>Sandia National Laboratories, Albuquerque, NM 87185, United States

Linear, branched, and star polymers exhibit distinctive rheological behavior, critical to their processing, depending on their topology. Early studies have shown that the effects of branches differ below and above the entanglement length and branches on the length scale of the entanglement length of the backbone results in increased viscosity. Using coarse grained molecular dynamics simulations we study the effects of degree of branching, including their length and density on the rheology of entangled polyethylene melts, with branch lengths above and below the entanglement length while the branching density is varied. Our coarse grained model are able to capture the flow properties observed by experimental studies and provide fundamental new correlations between branching length-densities and rheology for entangled branched polymers. As expected branched polyethylene chains diffuse slower than their linear analogs. For polymer melts with same  $M_w$ , diffusion is predominantly governed by the branch length and only slightly affected by the branching density. Beyond the new model for coarse grained of branched polymers, this study has provided new insight into a long standing challenges in polymer rheology.

Wednesday 10:40 Plaza I

PM16

### Relating chain conformations to extensional stress in entangled polymer melts

Thomas C. O'Connor<sup>1</sup>, Nicolas J. Alvarez<sup>2</sup>, and Mark O. Robbins<sup>3</sup>

<sup>1</sup>Harry S. Truman Fellow, Sandia National Laboratory, Albuquerque, NM 87123, United States; <sup>2</sup>Chemical Engineering, Drexel University, Philadelphia, PA 19104, United States; <sup>3</sup>Physics & Astronomy, Johns Hopkins University, Baltimore, MD 21218, United States

Nonlinear extensional flows are common in polymer processing but remain challenging theoretically because dramatic stretching of chains deforms the entanglement network far from equilibrium. Here, we present coarse-grained simulations of extensional flows in entangled polymer melts for Rouse-Weissenberg numbers  $Wi=0.06-52$  and Hencky strains  $>6$ . Simulations reproduce experimental trends in extensional viscosity with time, rate and molecular weight. Studies of molecular structure reveal an elongation and thinning of the confining tube with increasing  $Wi$ . The rising stress is quantitatively consistent with the decreasing entropy of chains at the equilibrium entanglement length. Molecular weight dependent trends in viscosity are related to a crossover from the Newtonian limit to a high rate limit that scales differently with chain length. Stress relaxations from steady state reveal chains rapidly retract and recover their equilibrium tube diameter even when chain primitive paths are fully aligned and do not intersect. Contrary to some geometric models of entanglement, our results suggest the degree of chain confinement is independent of the orientation of the entanglement network.

Wednesday 11:05 Plaza I

PM17

**Probe rheology simulation of heavily entangled polymer melts**Pouria Nourian<sup>1</sup>, Rafikul Islam<sup>1</sup>, Nestor Valadez-Perez<sup>2</sup>, Tsutomu Indei<sup>3</sup>, Jay D. Schieber<sup>2</sup>, and Rajesh Khare<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Texas Tech University, Lubbock, TX, United States;* <sup>2</sup>*Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL, United States;* <sup>3</sup>*Global Station for Soft Matter, Hokkaido University, Sapporo, Hokkaido, Japan*

Probe microrheology has emerged as a reliable experimental technique to measure viscoelastic properties of a complex medium. We have developed a simulation analog of experimental probe microrheology that combines molecular dynamics (MD) simulations with the inertial generalized Stokes-Einstein relation (IGSER) to predict the viscoelastic properties of soft matter. In previous work, it was shown that the viscoelastic moduli of unentangled ( $N < N_e$ ) and weakly entangled ( $N \sim 2N_e$ ) polymer melts as determined by our probe rheology simulation technique are in good agreement with those obtained from conventional simulation methods such as nonequilibrium MD (NEMD) simulations and the Green-Kubo formalism. Contrary to theoretical expectations, good agreement between probe rheology and bulk rheology results was also achieved using a probe particle whose size was smaller than the characteristic length scale (i.e. entanglement spacing) of the medium. To investigate this aspect further, we have applied our probe rheology simulation technique to heavily entangled polymer melts. Specifically, the technique is applied to polymer melts with  $N \sim 20N_e$  using probe particles of different sizes to investigate the interplay between the probe particle size and the entanglement spacing of the polymer. Simulation results are discussed in the context of literature theories of particle motion in an entangled polymer melt.

Wednesday 11:30 Plaza I

PM18

**Attempts to coarse grain a slip-link model to a tube model**Konstantin Taletskiy and Jay D. Schieber*Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States*

A recent comparison between experiments and theories for the dynamic modulus of linear/star-branched entangled polymer blends revealed that tube models were unable to describe simultaneously two different sets of data. Both the branch-on-branch (BoB) computer algorithm, and the hierarchical model were used with various sets of parameter values. While one set of values could describe one data set, it failed to describe the other. On the other hand, the discrete slip-link model (DSM) was able to describe both sets simultaneously, using parameters determined for monodisperse linear chains only. Since the slip-link level of description of entanglements is more detailed than that for tubes, it is computationally more expensive. Therefore, it might be useful to explore whether tube models can be repaired with information gleaned from slip-link models. Or, put another way, can slip-links be further coarse grained to develop a tube model that agrees with the experiment? Here we present evidence that tube models and slip-link models are not compatible. First, we show that they predict different scaling of the longest relaxation time of star-branched chains with and without constraint dynamics. Furthermore, coarse graining of the DSM to create a modified tube description fails to reproduce the longest relaxation time scaling of the detailed model. Repair of the tube model does not seem possible.

## Symposium PG Polyelectrolytes, Self-assembling Systems & Gels

Organizers: Nick Virgilio and Lilian Hsiao

Wednesday 9:50 Bellaire

PG9

**A direct correlation between the evolution of microstructure and recoverable strain in wormlike micellar solutions**Ching-Wei Lee and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Combining in-situ time-resolved small angle neutron scattering (SANS) and dynamic shear rheology, we demonstrate that the evolution of micellar segmental alignment is well correlated with the recoverable strain. The shear-induced alignments in both velocity-gradient and velocity-vorticity planes are shown to be dictated by the recoverable strain, independent of the imposed frequency. The micellar system exhibits a distinct sequence of physical processes under large amplitude oscillatory shear (LAOS) that begins at small recoverable strains with an interval of linear viscoelasticity, before transitioning to an interval of softening/thinning as the recoverable strain increases, and then recoiling as the recoverable strain decreases. This clearly identifiable sequence takes place twice per oscillation. While LAOS responses are typically viewed as being somehow intermediate cases, we demonstrate that information regarding both axes of Pipkin space, which consist of the steady-state flow curve and the linear-regime frequency sweep, can be obtained *within* the response to LAOS.

In addition to a clear interpretation of the shear stress response, we also investigate the normal stress response as a function of the transient recoverable strain. The first normal stress difference shows an open butterfly shape when plotted against the total strain, but shows a simple closed parabola when plotted against the recoverable strain. We observe minimum normal stress at zero recoverable strain and a normal stress that increases quadratically with the recoverable strain. This work provides a physical and straightforward path to further explore the rheological and microstructural evolutions of self-assembled and polymeric materials under flow.

Wednesday 10:15 Bellaire

PG10

**Tracking wormlike micelle topology during steady and transient shear flows with Dielectric RheoSANS**John K. Riley<sup>1</sup>, Jeffrey J. Richards<sup>1</sup>, Norman J. Wagner<sup>2</sup>, and Paul D. Butler<sup>1</sup><sup>1</sup>NCNR, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States; <sup>2</sup>University of Delaware, Newark, DE, United States

Topology and branching play an important but poorly understood role in controlling the mechanical and flow properties of worm-like micelles (WLMs). To address the challenge of characterizing branching during flow of WLMs, dielectric spectroscopy, rheology, and small-angle neutron scattering (Dielectric RheoSANS) experiments are performed simultaneously to measure the evolution of conductivity, permittivity, stress, and segmental anisotropy of reverse WLMs. Reverse WLMs are comprised of the phospholipid surfactant lecithin dispersed in oil with water solubilized in the micelle core. Their electrical properties are independently sensitive to the WLM topology. To isolate the effects of branching, Dielectric RheoSANS is performed on WLMs in n-decane, which exhibit a continuous branching transition for water-to-surfactant ratios above the maximum in zero-shear viscosity. Unbranched WLMs in n-decane exhibit only subtle decreases in their electrical properties under flow that are driven by chain alignment and structural anisotropy in the plane perpendicular to the electric field and incident neutron beam. These results are in qualitative agreement with additional measurements on a purely linear WLM system in cyclohexane despite differences in breakage kinetics and a stronger tendency for the latter to shear band. In contrast, the branched micelles in n-decane (higher water content) undergo non-monotonic changes in permittivity and larger decreases in conductivity under flow, revealing that branch-breaking plays a critical role in relieving stress in the early stages of shear thinning. Our approach provides the first direct signatures of changes in branching and connectivity during flow of WLMs. We will discuss experiments on WLMs undergoing steady-shear and large amplitude oscillatory shear (LAOS) flows. In the latter, structure-dielectric relationships allow us to track anisotropy through the electrical properties, which reveals rich information on dynamic structure during periods of fast transient stress response.

Wednesday 10:40 Bellaire

PG11

**Rheological and alignment transitions in wormlike micelle solutions**Javen Weston<sup>1</sup>, Katie M. Weigandt<sup>2</sup>, and Steven Hudson<sup>3</sup><sup>1</sup>Chemical Engineering, University of Tulsa, Tulsa, OK 74104, United States; <sup>2</sup>Center for Neutron Research, NIST, Gaithersburg, MD 20899, United States; <sup>3</sup>Polymers and Complex Fluids Group, NIST, Gaithersburg, MD 20899, United States

RheoSANS experiments were used to track segmental alignment in semi-dilute wormlike micellar solutions. In these experiments a peak in segmental alignment was observed at a certain shear rate, above which a relatively sharp decrease in alignment is observed. The transition appears to be the result of an elastic instability due to the curved streamlines present in the Taylor-Couette geometry used for RheoSANS experiments. The phenomenon was investigated using a variety of sample geometries and the alignment transition was seen to follow the Pakdel-McKinley criterion predicting flow instability for viscoelastic fluids. Interestingly, similar peaks in segmental alignment are observed with these samples in another flow geometry; a microfluidic slit rheometer that allows for simultaneous SANS of samples undergoing Poiseuille flow. In this flow cell a peak in alignment is observed in the near-wall region of the slit where the maximum shear rate is observed. Temperature also strongly affects the behavior of the fluid and can be used to shift the critical shear rate where the transition occurs. Here, we present work investigating the cause of the observed transitions in fluid structure and rheology and how various factors affect that transition in order to provide insight into the structure-property relationship in the high shear rate regime for this commercially-relevant system. Understanding the visco-elastic properties and flow induced structure of these micelles is beneficial for their use in personal care, oil recovery, and other applications. The system studied here is a useful model, since the micelle alignment is relatively easy to interpret and the formulation is similar to commercial consumer cleansers.

1) P. Pakdel and G.H. McKinley. "Elastic Instability and Curved Streamlines," Phys. Rev. Lett. 1996. 2459-2462. 2) J.S. Weston, D.P. Seeman, D.L. Blair, P.F. Salipante, S.D. Hudson, K.M. Weigandt. "Simultaneous slit rheometry and in situ neutron scattering," Rheo. Acta, 2018. 241-250.

Wednesday 11:05 Bellaire

PG12

**Dissolution kinetics in tangential fluid flow across the interface of micellar gels**Miriam Rafailovich<sup>1</sup>, Juyi Li<sup>1</sup>, Clement Marmorat<sup>2</sup>, Eyal Zussman<sup>3</sup>, Ishi Talmon<sup>4</sup>, Naama Koifman<sup>4</sup>, Jiang Jialong<sup>2</sup>, and Dilip Gersappe<sup>2</sup><sup>1</sup>Stony Brook University, Stony Brook, NY 11794-2275, United States; <sup>2</sup>Stony Brook University, Stony Brook, NY 11794-2275, United States; <sup>3</sup>Mechanical Engineering, Technion Israel Institute of Technology, Haifa, NY 11803, United States; <sup>4</sup>Chemical Engineering, Technion Israel Institute of Technology, Haifa, Israel

Polaxomers have been proposed as biomimetic substitutes for physiological gels. Concern regarding their ability to resist swelling under fluid flows has impeded their implementation. Using a combination of techniques including cryo TEM and rapid X-ray imaging, we found that rapid flow rates stabilized the gels against dissolution. Energy balance calculations confirmed that disentanglement of individual micelles was not possible at time scales faster than the reptation time when the system response was that of a solid which dissipated the hydrodynamic force field via cooperative deformation.

Wednesday 11:30 Bellaire

PG13

**Salt effects on the rheology of semidilute polyelectrolyte solutions**Antonio Perazzo, Emre Turkoz, Craig B. Arnold, and Howard A. Stone*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, United States*

Polyelectrolytes are ubiquitous charged macromolecules and are often dispersed in aqueous media. Being charged, the addition of salts/electrolytes changes the microstructure of the suspended polymers as a function of the salt concentration, which in turn affects the mechanical properties of the solution. Despite advances in theory, simulations and many experimental measurements, it is unknown how the mechanical properties of these macromolecules are affected by different types of salts at the same concentration. Here, we show that different kinds of salts at a fixed concentration can be used to tune viscoelastic properties of a xanthan gum solution in a broad range of relaxation times. These results can be insightful towards enhanced oil recovery and turbulent drag reduction applications, where polyelectrolytes are present and their rheology plays a key role.

**Symposium SG****Solids, Composites & Granular Materials**

Organizers: Jonathan Seppala and Denis Rodrigue

Wednesday 9:50 Post Oak

SG1

**Emergence and persistence of flow inhomogeneities in the yielding and fluidization of dense soft solids**Vasishth Vishwas<sup>1</sup>, Gabrielle Roberts<sup>2</sup>, and Emanuela Del Gado<sup>3</sup><sup>1</sup>*Lyph, Universite Grenoble Alpes, Grenoble, France;* <sup>2</sup>*Physics, Yale University, New Haven, CT, United States;* <sup>3</sup>*Georgetown University, Washington, DC, United States*

The response to shear of dense soft solids features a stress overshoot and a persistent shear banding before reaching a homogeneously flowing state. In 3D large scale computer simulations of a model non-Brownian jammed suspension we analyze the time required for the onset of homogeneous flow, the normal stresses and the particle packing at different shear rates with and without confinement, finding that the stress overshoot and flow inhomogeneities are controlled by the presence of overconstrained microscopic domains in the initially solid samples. Being able to identify such domains in our model by prevalently icosahedrally packed regions, we show that they allow for stress accumulation during the stress overshoot and that their structural reorganization controls the emergence and the persistence of the shear banding.

Wednesday 10:15 Post Oak

SG2

**3D simulation of dense granular flow in a rotating drum**Angelica Maria G. Arseni, Gaetano D'Avino, Francesco Greco, and Pier Luca Maffettone*Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, Università degli Studi di Napoli Federico II, Napoli, Italy*

Granular materials, i.e., conglomerates of macroscopic solid particles in contact, are ubiquitous in our world. They are widely used in industry as well as in nature; granular materials have numerous applications in industry, i.e. in pharmaceutical, food, polymers, petrochemical processing, and in geophysics for the evaluation of natural hazards such as landslides and pyroclastic flows. When subjected to external forces, granular materials exhibit complex pattern-forming behaviours; numerical simulations can then provide a useful tool to understand the physics underlying the dynamics of these materials. In most of the works available in the literature, the commonly adopted numerical approach to study granular materials is the Discrete Element Method (DEM), where the material is modeled as an assembly of rigid particles, and the interactions among particles are explicitly considered. Although DEM has the advantage to describe the discrete nature of the flow, a relatively limited number of particles can be managed. To overcome this drawback, a continuum approach is desirable. In this work, we present 3D Finite Volume (FV) simulations of dense granular flow inside a rotating cylinder, adopting the visco-plastic Jop-Forterre-Pouliquen constitutive model [1] for the granular medium stress tensor. The effects of the cylinder aspect ratio, the drum angular velocity, and the particle dimensions (as a parameter in the constitutive equation) are investigated. The results obtained from our simulations for free-surface shape and velocity, and for thickness of the flowing layer, are also compared with experimental results available in the literature [2-3].

[1] Jop, P., et al., (2006), *Nature*, 441 (7094), 727. [2] Ding, Y. L., et al., (2001), *Chemical Engineering Science*, 56, 1769-1780. [3] Alexander, A., et al., (2002), *Powder Technology*, 126 (2), 174-190.

Wednesday 10:40 Post Oak

SG3

**Thermal and rheological analysis of polystyrene-grafted silica nanocomposite: Effect of graft length on absolute heat capacity and rubbery plateau modulus**Nazam U. Sakib, Yung P. Koh, and Sindee L. Simon*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The thermal and rheological properties of two polystyrene-grafted silica nanocomposites having different graft lengths are investigated. The nanocomposites are both matrix free, consisting only of the neat grafted silica particles, one with grafts of 35 kg/mol and one with grafts of 112 kg/mol. Properties are compared to those of neat polystyrenes of similar molecular weights. DSC studies revealed a T<sub>g</sub> increase of approximately 1 K for the nanocomposites and a decrease of approximately 5 to 7% in absolute heat capacity. The step change in heat capacity at T<sub>g</sub> ( $\Delta C_p$ ) decreases by approximately 13% for the nanocomposites indicating a reduction in the fraction of polymer undergoing the glass transition. The

viscoelastic properties of the nanocomposite samples also differ compared to the neat analogs. In addition to a slight shift of the nanocomposite  $G'$  vs.  $\omega$  master curves lower frequencies associated with the  $T_g$  increase, the terminal viscous rheological behavior is not observed for the nanocomposites. The rubbery plateau modulus  $G_{N,0}$  is found also to decrease slightly for the 35 kg/mol grafts, whereas for the 112 kg/mol grafts, it increases by approximately nine (9) fold.

Wednesday 11:05 Post Oak

SG4

### **Structural evolution of grafted-nanoparticles in shear flow**

Ramanan Krishnamoorti

*Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77004, United States*

Polymer-grafted nanoparticles, at high grafting densities, arrange into highly ordered crystalline arrangements. The linear viscoelastic properties of such hybrids demonstrate many similarities to colloidal suspensions and star polymers. However, their viscoelastic response to strong shear flows is significantly different. Specifically, these systems demonstrate strong shear-thinning character. Direct structural probes such as in-situ x-ray scattering demonstrate the formation of slip planes that are possibly responsible for the strong shear-thinning character.

Wednesday 11:30 Post Oak

SG5

### **Yielding, strain hardening, and necking in LLDPE/SEPS rubber bilayer laminates**

Rahul Ramachandran<sup>1</sup>, Hariharakrishnan Sankaran<sup>2</sup>, Steven Abramowitch<sup>3</sup>, Spandan Maiti<sup>3</sup>, and Sachin S. Velankar<sup>2</sup>

<sup>1</sup>*Dept. of Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States;* <sup>2</sup>*Dept. of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States;* <sup>3</sup>*Dept. of Bioengineering, University of Pittsburgh, Pittsburgh, PA, United States*

Semicrystalline plastics often show necking and drawing behavior in tension. The necking behavior is attributable to the fact that such plastics possess a yield stress. The drawing behavior is attributable to post-yield strain hardening that stabilizes the neck, thus allowing the neck to propagate. In sharp contrast, rubbery materials do not show necking, but instead stretch homogeneously. We examine the behavior of bilayer laminate composites of linear low density polyethylene (LLDPE) and styrene-ethylene-propylene-styrene (SEPS) rubber to test the extent to which the SEPS can modify the tensile necking behavior of the LLDPE. Video recordings of tensile tests on dog-bone shaped samples were analyzed by a Digital Image Correlation (DIC) technique to quantify the degree of non-homogeneity in deformation. The LLDPE showed severe necking with a natural draw ratio exceeding 5. Upon bonding it to a rubber layer, the natural draw ratio reduced significantly. With a sufficiently large SEPS thickness, the neck was almost completely eliminated and the sample reverted to nearly-homogeneous deformation.

We present a 1D model for the mechanics in which the force within the bilayer laminate is treated as a sum of the force of the two layers: a rubber layer obeying the Mooney-Rivlin equation, and an elastoplastic layer obeying the Haward model (which is a sum of a yield stress and a neo-Hookean term). The resulting force equation is analyzed as per the Maxwell equal-area construction to predict the natural draw ratio and the draw stress. The model predicts the decrease in natural draw ratio and the elimination of necking as rubber thickness increases, consistent with experiments. Further insights from 3D FEM simulations will also be presented.

## **Symposium ET**

### **Advanced Experimental Techniques/Methods in Rheology**

Organizers: Kalman Migler and Simon Rogers

Wednesday 9:50 San Felipe Room

ET14

### **High-pressure linear viscoelasticity measurements of polymer solutions and gels**

Kimberly A. Dennis<sup>1</sup>, Yan Gao<sup>2</sup>, Alhad Phatak<sup>2</sup>, and Eric M. Furst<sup>1</sup>

<sup>1</sup>*University of Delaware, Newark, DE 19716, United States;* <sup>2</sup>*Schlumberger, Sugar Land, TX, United States*

Enhanced oil recovery (EOR) fluids are polymer solutions and gels that are designed to transport and suspend solids, reduce friction, and prevent fluid loss. EOR fluid performance depends on its viscosity and elastic modulus. To address the need to characterize the viscoelasticity of EOR fluids under operating conditions, we developed a passive microrheology experiment capable of generating pressures up to 200 MPa. The apparatus incorporates a sealed steel alloy sample chamber with dual sapphire windows into a diffusing-wave spectroscopy (light-scattering) experiment. The measured light intensity correlation arising from the Brownian motion of polystyrene probe particles dispersed in the sample is interpreted using the Generalized Stokes-Einstein Relation (GSER) to determine the material creep compliance. We validate this high-pressure microrheology instrument by measuring the increase in viscosity of 1-propanol aqueous solutions and extend the measurement to EOR fluids containing poly(vinyl) alcohol polymer and borate as a physical crosslinker. Sample loading methods were designed to prevent the introduction of bubbles, which inhibits pressurization by increasing the sample compressibility. However, these methods were limited to low moduli samples that could be easily loaded with a syringe and needle. New methods for increasing the operating regime to nonergodic gel samples as well as higher temperatures have been developed. We investigate the effect of pressure on the crosslink density and rheological properties at frequencies up to 1 MHz and pressures to 200 MPa.

Wednesday 10:15 San Felipe Room

ET15

**Non-equilibrium micro-rheology of a model soft colloidal glass**Qi Li<sup>1</sup>, Xiaoguang Peng<sup>2</sup>, and Gregory B. McKenna<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States;* <sup>2</sup>*Chemical & Biomolecular Engineering, University of Connecticut, Storrs, CT, United States*

Micro-rheology has proven to be a powerful tool in measuring viscoelastic properties for colloidal systems [1,2], and is known to capture the equilibrium dynamics in colloids approaching their concentration glass transition [3]. In this study, the diffusing wave spectroscopy (DWS)-based micro-rheology was used with different optical geometries (backscattering and transmission) as well as different sample thicknesses, which enable us to probe the system dynamics at different length scales [2]. The object is to explore more in non-equilibrium dynamics and address the range of utility of DWS as a micro-rheological method. A thermo-sensitive PS-PNIPAM/AA model colloidal system was investigated in equilibrium and non-equilibrium states by temperature-jump induced volume-fraction jump experiments. We find that in the case of the equilibrium state, the dynamics is insensitive to the optical geometry (backscattering and transmission) and length scales; whereas in the non-equilibrium state, significant differences in the measured dynamics is observed for the different geometries and length scales. The difference in non-equilibrium behaviors for different length scales provides a possibility to examine more closely the aging mechanism for colloidal glasses. Furthermore, the fact that length scale effects were observed only in non-equilibrium conditions indicates that, while dynamic heterogeneity is associated with the non-equilibrium dynamics of colloidal glasses, it does not seem to be the controlling factor for the colloidal glass transition process.

[1] J. Liu, M. L. Gardel, K. Kroy, E. Frey, B. D. Hoffman, J. C. Crocker, A. R. Bausch, and D. A. Weitz. *Phys. Rev. Lett.* 96, 118104 (2006). [2] W. Brown. *Dynamic Light Scattering: The Method and Some Applications*. Oxford Univ. Press, Oxford. 1993 [3] Q. Li, X. Peng, and G. B. McKenna. *Soft Matter* 13, 1396 (2017).

Wednesday 10:40 San Felipe Room

ET16

**Measuring the mechanical properties of soft particles through microfluidics**Massimiliano M. Villone<sup>1</sup>, Janine K. Nunes<sup>2</sup>, Howard A. Stone<sup>2</sup>, and Pier Luca Maffettone<sup>1</sup><sup>1</sup>*Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, Università degli Studi di Napoli Federico II, Napoli, Italy;*<sup>2</sup>*Department of Mechanical and Aerospace Engineering, Princeton University, princeton, NJ 08544, United States*

Suspensions carrying deformable inclusions are ubiquitous in nature, scientific, and industrial applications. In particular, elastic particles are a good model for microgel beads, swollen starch granules, and cells. High-throughput characterization of the mechanical properties of soft particles would be, then, of great interest. Recently, a non-invasive microfluidic technique has been developed for the measurement of the interfacial tension between two immiscible liquids [1]. We have adapted such technique to the case of soft solid beads, in such a way as to provide a non-invasive microfluidic technique for the measurement of the mechanical properties of deformable particles. We have designed a cylindrical microfluidic channel with a cross section reduction in which initially spherical soft beads are made to flow suspended in a Newtonian carrier. By recording in real time the deformation of a particle as it goes through the constriction, it is possible to get a measure of its elastic modulus through of a theoretically derived-correlation. We provide both experimental and numerical validation of our design.

[1] S. D. Hudson et al., *Appl. Phys. Lett.*, 2005, 87, 081905

Wednesday 11:05 San Felipe Room

ET17

**Pushing the boundaries of passive microrheology with artificial thermal noise**

Shalaka Kale and Joseph R. Samaniuk

*Colorado School of Mines, Golden, CO 80401, United States*

Viscoelastic properties of many natural and synthetic complex materials vary internally at the micrometer scale, ultimately influencing the material properties and function. For example, heterogeneity in microstructure affects intra-cellular translocation of nutrients and biomolecules through lipid membranes, and the function of hydrogel-based scaffolds is affected by local variations in viscoelastic properties. Characterizing the viscoelastic response of such complex materials at small length scales can be accomplished with passive microrheology. It is a tool that employs colloidal particles as probes to infer viscoelasticity from their Brownian motion. Passive microrheology combined with video microscopy can be used to resolve micrometer-scale variations in viscoelasticity, but the measurement regime is limited to relatively low moduli. For instance, a probe particle of 1  $\mu\text{m}$  diameter at room temperature tracked with 10 nm spatial resolution can be used to measure a maximum complex modulus on the order of  $10^0$  Pa. Thus, this form of passive microrheology is unsuitable for resolving rheological properties of materials like alginate-chitosan hydrogels that have complex moduli that vary from  $10^1$  to  $10^3$  Pa. To overcome this limitation, we use active microrheology in the form of electromagnetic coils driven by an artificial noise signal, and superparamagnetic particles as probes. The approach is to generate an in-silico red-noise signal, amplify it and send it as current through the coils to drive the particles 'randomly' with energies exceeding  $k_B T$  by orders of magnitude. The resulting fluctuations of the probe are captured with particle tracking software and presented as mean squared displacements. We will discuss the merits of naïve application of the Generalized Stokes Einstein Relation (GSER) for reporting viscoelastic properties with this approach, and the consequences of violating the fluctuation-dissipation theorem.



Wednesday 11:30 San Felipe Room

ET18

**Novel use of the van Gorp-Palmen Plot: New insights into polymer dynamics**Zhiyuan Qian and Gregory B. McKenna*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The van Gorp-Palmen plot (vGP) [van Gorp, M. and Palmen, J., Rheology Bulletin, 1998, 67, 5-8.] was originally proposed to verify the validity of Time-Temperature Superposition. It was found to be sensitive to polymer molecular weight, polydispersity, and structure. In the current work, a novel use of the vGP plot is proposed after reexamination of the vGP plot by compiling literature data for polymer melts with different topological structures: linear (pure and blend), ring, comb, and bottlebrush. A new parameter: the reciprocal of complex modulus at the first minimum moving from the terminal regime is defined and compared with the steady-state recoverable compliance. Results show that these two parameters while related to each other, as they follow similar dependences on the molecular weight, weight fraction of high molecular weight content and backbone concentration, there are also differences. The work we shown here expands the application of vGP plot and provides new insights into understanding polymer dynamics.

**Symposium FE****Foams, Emulsions & Interfacial Rheology**

Organizers: John Frostad and Joseph Samaniuk

Wednesday 9:50 Tanglewood

FE5

**Viscoelasticity of a drying emulsion**H. Henning Winter*Chemical Engineering, Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

Rheological patterns will be shown for an emulsion of lower and lower water content. The data originate from two types of experiments: (1) A novel technique which allows in-situ small angle oscillatory shear (SAOS) during drying. The mutation number provides a criterion for the admissibility of individual data points. (2) Stable samples of well-known water content will be characterized by SAOS. Comparison of the two data sets allows further insight, which will be discussed at the meeting.

Wednesday 10:15 Tanglewood

FE6

**Field-induced control of magnetic emulsions rheology**Lucas Hildebrand Pires da Cunha<sup>1</sup>, Ivan Rosa de Siqueira<sup>2</sup>, and Taygoara Felamingo de Oliveira<sup>1</sup>*<sup>1</sup>Department of Mechanical Engineering, University of Brasília, Brasília, DF 70910-900, Brazil; <sup>2</sup>Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

It is studied the possibility of controlling the rheology of magnetic emulsions by the application of magnetic fields. For this purpose, numerical simulations in a two-dimensional perspective for a ferrofluid droplet suspended in a non-magnetic liquid under the effect of a shear flow and external magnetic fields are done. The absence of electrical fields and magnetic field variation in time possibility the reduction of the Maxwell equations to the magnetostatic limit. Also, it is considered the hypothesis of superparamagnetism for the magnetizable droplet. The Projection method is applied, decoupling the velocity and pressure solutions, while the Level-Set method is used to capture and compute the droplet geometry. The droplet inclination and emulsion viscosity are measured in function of the magnetic field, varying it in intensity and direction. We found a strong influence of the magnetic field on the droplet inclination and consequently on the emulsion viscosity. The droplet tends to get aligned with the field. The great alignment between the droplet and the flow reduces the emulsion viscosity, while the misalignment increases it. Therefore, the emulsion viscosity can be, indeed, increased and reduced by the application of external fields.

Wednesday 10:40 Tanglewood

FE7

**Breakup of magnetic drops under simple shear and magnetic field**Taygoara F. Oliveira<sup>1</sup> and Lucas H. Cunha<sup>2</sup>*<sup>1</sup>Mechanical Engineering, University of Brasilia, Brasília, Brazil; <sup>2</sup>Mechanical Engineering, University of Brasília, Brasília, Brazil*

Emulsion is a biphasic mixture of two immiscible viscous liquids which one is dispersed in the other as droplets. Generally, emulsions are produced by droplets rupture processes in a pair of fluids, depending the dispersed phase (droplets) and the continuous phase (base fluid). Controlling the droplets' sizes is an essential task in production processes. The breakup of a single drop depends on the capillary number, viscosity ratio and Reynolds number. This work aims to physically understand how the application of an external magnetic field can interfere on this process and how it could help having a better control of it. To this end, the level-set method is used in to simulate magnetic drops under combined action of simple shear flow and external constant magnetic field. The projection method is applied in order to decouple the pressure and velocity fields, which are computed using the Finite Difference Method. By applying the magnetic field on the velocity direction, the drop tends to align with the velocity field reducing the effective shear action on it, avoiding or delaying rupture. In the other hand, when the magnetic field is applied on the

velocity gradient direction, the drop elongates and inclines in such way it become more exposed to shear, being more susceptible to breaking up. It was also noticed that the magnetic field has an influence on the volume ratio of the resultant drops.

Wednesday 11:05 Tanglewood

FE8

### **Effect of droplet size and volume fraction on rheology of nanoemulsions**

Neda Sanatkaran and Reza Foudazi

*Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

In this work, we investigated the viscoelastic and flow properties of oil-in-water nanoemulsions to verify rheological scaling models of macroemulsion systems. Emulsions were prepared using silicone oil with different average droplet sizes (ranging from 1  $\mu\text{m}$  to below 100 nm) dispersed in sodium dodecyl sulfate solution. Droplet size distributions were narrow and remained unchanged for all the samples. Viscoelastic responses and yielding of emulsions were examined as a function of dispersed phase volume fractions (35 - 65 %) for each of the droplet sizes. The range of volume fractions for the samples was obtained via an evaporation-dilution technique. Laplace pressure of droplets was used to make the dynamic moduli dimensionless. Results revealed that below a specific droplet size the dimensionless elastic moduli of the emulsions overlap in the concentrated region. This specific droplet size corresponds to the point where the yielding behavior of the nanoemulsions no longer obeyed the macroemulsions scaling model.

Wednesday 11:30 Tanglewood

FE9

### **Connecting bubble growth during foaming with the mechanics of the solid foam**

Christos Mitrias<sup>1</sup>, Thijs Egelmeers<sup>1</sup>, Nick Jaenssen<sup>1</sup>, Martien A. Hulsen<sup>2</sup>, and Patrick D. Anderson<sup>3</sup>

*<sup>1</sup>Eindhoven University of Technology, Eindhoven, The Netherlands; <sup>2</sup>Polymer Technology, Eindhoven University of Technology, Eindhoven, The Netherlands; <sup>3</sup>Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands*

Elastomeric foams are widely used in many different types of applications. Studying the evolution of the microstructure experimentally can be extremely challenging. Different material properties are of interest in each application, from energy absorption during impact events to thermal and sound insulation. All of these properties are governed by the microstructure and the properties of the material matrix. In this paper we show that direct numerical simulations give insight on the dynamics and rheology during the creation of the gas bubbles, until the solidification into a cellular morphology. The foam is described by a representative volume element (RVE), where a small number of bubbles is randomly distributed. Using this approach, the RVE can describe the bulk behaviour of the foam, while remaining computationally tractable. We show that the resulting microstructure can be used directly in simulations of solid mechanical testing and yield the mechanical properties of the foam.

## **Symposium NF Non-Newtonian Fluid Mechanics & Flow Instabilities**

Organizers: Aditya Khair and Christian Clasen

Wednesday 9:50 Plaza II

*Keynote* NF14

### **Using SAOS, LAOS and narrow gap rheology to better understand changes to food structure during oral processing**

Michael W. Boehm and Stefan Baier

*PepsiCo., Hawthorne, NY 10532, United States*

Eating can be pleasurable or displeasing: the experience is dependent upon a complex web of simultaneous and sequential chemical and physical processes. For scientist working in R&D at food companies and ingredient manufacturers, new product development based on a rational design philosophy involves translating structure-function relationships-gained by probing the fundamental physics of eating-into final product design. One driver of research has been the consumers' desire for "healthier" options, i.e., foods with less fat, sugar and salt. Using the potato chip as an example, we have learned, through sensory testing, that the experience of eating baked chips and fried chips is different. Considering the physics of eating as comminution and mixing with saliva, bulk bolus deformation and high shear confined flow between tongue and other oral surfaces, we use SAOS, LAOS and high shear narrow gap flow to probe the dynamics of non-destructive and destructive deformations of simulated potato chip boluses. In this talk, we will present results from these techniques and discuss implications for oral processing and new product development of similarly starch-based solid snack foods.

Wednesday 10:15 Plaza II

NF15

### **Intrinsic nonlinearity in oscillatory shear from the corotational Maxwell fluid**

Alan J. Giacomin<sup>1</sup>, Pongthep Pongthong<sup>2</sup>, Chaimongkol Saengow<sup>1</sup>, and Chanyut Kolutawong<sup>2</sup>

*<sup>1</sup>Chemical Engineering, Queen's University, Kingston, ON K7L 3N6, Canada; <sup>2</sup>Mechanical and Aerospace Engineering Department, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand*

The ratio of the shear stress amplitudes of higher harmonics to the first, called relative intensities, is a widely established way of characterizing materials and of representing large-amplitude oscillatory shear flow (LAOS) measurements. If we divide these relative intensities by appropriate

powers of strain amplitude, we define intrinsic nonlinearities. In their limits of vanishing strain amplitude, these relative intensities give relative intensity parameters. Here, we arrive at an exact analytical solution for the  $m$ th intrinsic nonlinearity for the shear stress of a corotational Maxwell fluid and, for example, evaluate it for the first three harmonics (third, fifth and seventh). We then use the Spriggs relations to generalize these relative intensities and corresponding intrinsic nonlinearities to multimode. For consistency, we check the expansion of our results against the well-known first term in the expansion in powers of the strain amplitude [Appl. Rheol., 26, 53809 (2016)]. We also introduce an expansion of the intrinsic nonlinearity in the shear rate amplitude. Finally, we compare our generalized results, third-to-first and fifth-to-first relative intensities, with measurement on molten 1,4-cis-polyisoprene.

Wednesday 10:40 Plaza II

NF16

### **Visualization of chain dynamics of highly entangled shear-banding polymer solutions under large amplitude oscillatory shear (LAOS)**

Seunghwan Shin, Kevin D. Dorfman, and Xiang Cheng

*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States*

In contrast to well-entangled linear worm-like micelles, where the existence and the origin of shear-banding flows have been well established, the understanding of morphological and conformational changes that accompany shear banding in entangled polymer solutions is still far from complete. Here, we analyze the shear profiles and polymer dynamics of well-entangled double-stranded DNA (dsDNA) under LAOS by combining a custom planar Couette shear cell and a high-resolution confocal microscope. Under LAOS at sufficiently high Weissenberg number ( $Wi$ ), the velocity profiles display clear evolution from linear to shear-banding flows. Interestingly, in the shear-banding flows, the edge disturbance exhibits an unexpectedly long penetration length that is an order of magnitude larger than the gap thickness. To further investigate the microscopic structural origin of the shear banding, we study the dynamics and distribution of individual dsDNA chains in the shear banding flows. Analysis of the dynamics of DNA chains reveals spatially distinctive features, which provide insights into the origin of the two co-existing bands.

Wednesday 11:05 Plaza II

NF17

### **A new mechanism for shear banding of a thixotropic yield stress fluid**

Michela Geri<sup>1</sup>, Brice Saint-Michel<sup>2</sup>, Thibaut Divoux<sup>3</sup>, Sebastien Manneville<sup>4</sup>, and Gareth H. McKinley<sup>1</sup>

*<sup>1</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>Department of Chemical Engineering, Imperial College, London SW72AZ, United Kingdom; <sup>3</sup>MSE2, CNRS Bordeaux, CNRS-MIT, Cambridge, MA, United States; <sup>4</sup>Laboratoire de Physique, ENS Lyon, Lyon, France*

Shear banding is known to affect the flow of many complex fluids subject to simple viscometric flows. These fluids usually share a common feature in their underlying flow curve: a non-monotonic branch where the stress is a decreasing function of the shear rate. For thixotropic yield stress fluids this unstable branch usually spans between zero and a critical shear rate. Experiments performed on different systems, such as pastes and colloidal gels, show that steady-state banding occurs for any flows where the applied shear rate is smaller than this critical value and is characterized by an arrested band adjacent to a steady sheared region, while the stress measured during flow is constant and equal to the apparent yield stress. Here, we report on a new mechanism for steady-state shear banding observed in a thixotropic yield stress fluid for which the non-monotonic branch can be partially accessed during measurements of the flow curve. The fluid is made of a suspension of microscopic paraffin platelets in mineral oil at different concentrations. We perform rheometric tests in a bespoke Couette cell with roughened walls and a 1mm gap while measuring the local velocity field via ultrasonic velocimetry. The tests consist of decreasing shear rate steps of variable length and the stress response is recorded for the entire duration of each step. Results for different concentrations show the existence of two different critical shear rates corresponding to the local minimum and maximum observed in the flow curve. Below the first critical shear rate slip occurs close to the rotor, an arrested growing band appears close to the stator and the flowing region remains sheared at a constant shear rate. Below the second critical shear rate, the velocity field in the contracting flowing band is characterized by an inhomogeneous shear rate reminiscent of the flow field that develops in the presence of non-local effects. Based on these experimental observations we attempt to describe the velocity field using existing fluidity models.

Wednesday 11:30 Plaza II

NF18

### **Transient dynamics of the yielding transition in soft materials**

Gavin J. Donley<sup>1</sup>, John R. de Bruyn<sup>2</sup>, Gareth H. McKinley<sup>3</sup>, and Simon A. Rogers<sup>1</sup>

*<sup>1</sup>Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; <sup>2</sup>Physics and Astronomy, University of Western Ontario, London, Ontario N6A 3K7, Canada; <sup>3</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

A rigorously-defined metric that maps the transient yielding response of elastoviscoplastic materials is proposed and investigated. Motivated by linear viscoelastic theory for oscillatory deformations, the method utilizes the motion of an instantaneous phase angle between the stress and strain of the rheological response within deformation space to quantify the yielding transition. Principal component analysis demonstrates that this phase angle velocity is based on the natural description for a material response in deformation space. The responses of the Carreau model in its plastic-like state, and a Carbopol microgel are investigated as theoretical and experimental model yield stress fluids. Use of the phase angle velocity clearly identifies the yield transition as being gradual and distributed across the microstructural deformation mechanisms within the material. This approach provides a physically-motivated understanding of the processes occurring during yielding of elastoviscoplastic materials.



## Wednesday Afternoon

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Wednesday 1:30 Galleria I

SC32

#### **Towards a general constitutive model of dense frictional suspensions**

Abhinendra Singh<sup>1</sup>, Omer Sedes<sup>2</sup>, Sidhant Pednekar<sup>2</sup>, Morton M. Denn<sup>1</sup>, and Jeffrey F. Morris<sup>2</sup>

<sup>1</sup>*Levich Institute, City College of New York, New York, NY 10031, United States;* <sup>2</sup>*Department of Chemical Engineering, City College of New York, New York, NY 10031, United States*

The mechanism of shear thickening in dense suspensions has been shown to be consistent with a transition from lubricated rheology, where close interactions between suspended particles take place through a thin liquid film, to a frictional rheology, wherein particles experience frictional contacts. Particle simulations that led to this concept have been successful in quantitatively reproducing the non-Newtonian shear behavior of discontinuous shear thickening suspensions [1]. As a step towards developing a constitutive model for such materials, we extend the method presented by Wyart-Cates [2] for lubricated and frictional rheologies that is applicable to both shear and normal stresses for non-colloidal suspensions and demonstrate the agreement between such a model and the simulation results [3]. Through this approach, we develop a flow-state map of this material. The challenge of extension of this framework for constitutive modeling of colloidal suspensions remains. In order to guide the efforts to tackle this challenge, we examine the role of cohesive forces on the shear rheology of colloidal suspensions. This is achieved through the inclusion of interparticle repulsive and cohesive forces in addition to hydrodynamic and frictional forces that have been present in our particle simulations [4]. These simulations at low to the intermediate strength of cohesion show yield stress at low stress, followed by shear thinning and eventual shear thickening at high values of stress. For high strength of cohesion shear thickening is obscured. Including the details about yield stress and shear thinning, an extension to the shear thickening model to cohesive non-Brownian dense frictional suspension is proposed.

**References:** [1] Mari, R. et al., 2015 PNAS, 112(50), pp.15326-15330. [2] Wyart, M. and Cates, M.E., 2014 PRL, 112(9), p.098302. [3] Singh, A. et al., 2018, Journal of Rheology, 62(2), pp.457-468. [4] Pednekar et al., 2017, Soft Matter, 13(9), pp.1773-1779.

Wednesday 1:55 Galleria I

SC33

#### **Micromechanical modeling of heterogeneous suspensions**

Benjamin E. Dolata<sup>1</sup> and Roseanna N. Zia<sup>2</sup>

<sup>1</sup>*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States;* <sup>2</sup>*Chemical Engineering, Stanford University, Stanford, CA, CA 94305-4125, United States*

We present a theoretical study of the stress tensor in dilute heterogeneous suspensions. In such flows, the traditional volume averaging approach employed to compute the stress tensor in a statistically homogenous suspension is no longer generally valid; to overcome this limitation, we utilize a point-wise ensemble averaging method. In contrast with homogeneous suspensions, where the particle stress depends only on the integral of the stress interior to the particle, i.e. the stresslet and torque, the stress in heterogeneous suspensions depends on the first, second, and all higher-order moments of the stress interior to the particle. Using tensor decomposition techniques, we derived differential identities that allow transformation of these volume moments of the stress into surface moments of the hydrodynamic traction and fluid velocity. We show that the stress tensor in heterogeneous suspensions is symmetric in the absence of externally applied torques on the particles, in contrast with prior work. We derive constitutive equations for dilute suspensions of spherical particles, showing that spatial heterogeneity in the suspension breaks the usual isotropy of the constitutive equations, leading to new couplings that are forbidden by symmetry in homogeneous suspensions.

Wednesday 2:20 Galleria I

SC34

#### **High frequency stress contributions of colloidal dispersions: From hard to soft, from smooth to frictional**

Bram Schroyen<sup>1</sup>, Chiao-Peng Hsu<sup>1</sup>, Lucio Isa<sup>1</sup>, Peter Van Puyvelde<sup>2</sup>, and Jan Vermant<sup>1</sup>

<sup>1</sup>*Department of Materials, ETH Zürich, Zürich, Switzerland;* <sup>2</sup>*Department of Chemical Engineering, KU Leuven, Leuven 3000, Belgium*

Colloidal dispersions are an interesting class of materials that can display a wide range of rheological behavior such as the occurrence of a yield stress, shear thinning and shear thickening. Their rheological response is inherently viscoelastic as a result of Brownian relaxation, and is further governed by hydrodynamic and thermodynamic forces. High frequency rheology has proven very useful to study the local structure and interactions of colloidal dispersions up to high particle concentrations. In this work, a home-built piezo shear rheometer is used in parallel with a commercial device to perform frequency sweeps over an extended range. This allowed us to investigate the stress contributions at timescales much faster than the diffusional motion of the particles in the dispersion, or at very local length scales. Surface characteristics of the particles were varied in two different ways. First, dispersions of PMMA-g-PHSA particles with varying lengths of PHSA stabilizer were used to systematically vary the thickness of a repulsive thermodynamic layer with respect to the core radius. Second, model smooth and rough silica particles with well-

defined asperities were studied to determine the role of lubrication forces and frictional interactions from the topological effects. The high frequency stress response proves very sensitive to the dominant interparticle interactions that act locally. Identifying these local interactions plays an important role in understanding the nature of certain rheological phenomena, such as the onset of continuous and discontinuous shear thickening in colloidal dispersions.

Wednesday 2:45 Galleria I

SC35

### **Squeeze flow rheology of shear thickening suspensions**

Jose A. Ruiz-Lopez<sup>1</sup>, John Royer<sup>2</sup>, Mark Haw<sup>1</sup>, and Wilson Poon<sup>2</sup>

<sup>1</sup>*Chemical and Process Engineering, University of Strathclyde, Glasgow, Lanarkshire G1 1XJ, United Kingdom;* <sup>2</sup>*School of Physics and Astronomy, The University of Edinburgh, Edinburgh, United Kingdom*

Concentrated suspensions of particles with strong repulsive interactions typically exhibit a shear-thickening behavior. At relatively low concentrations, the viscosity increases continuously from a low-shear-rate plateau to a higher viscosity value at high shear rates. However, at high concentrations, the viscosity increases sharply and eventually the sample jams. This behavior has been recently explained in terms of “frictional contacts” between particles in experiments and simulations [1-2]. Understanding the underlying mechanisms of shear-thickening fluids is an important milestone in several industrial processes, often involving complex flows, as in extrusion. Hence, it is important understand the rheological properties of suspensions in extensional flows. In this work we studied the squeeze flow behavior of suspensions of corn starch in glycerol-water mixtures using a rough plate-plate geometry at constant compression rates. Results for Newtonian fluids showed that the normal force increases during compression and also with the compression rate. These results were fitted in terms of squeeze flow theories for no-slip boundary conditions and rough plates obtaining a similar viscosity as the viscosity of the fluid measured in shear flow. For suspensions, the obtained viscosity increases with the compression rate showing a continuous thickening at middle concentrations and discontinuous thickening at high concentrations. Viscosities in compression were higher than the viscosities obtained for shear flow at the same rate-of-deformation and the thickening onset rate was much lower in the compression case. However, the general form of the thickening response in squeeze flow is similar to that in shear, indicating that the frictional contact framework of thickening in shear also applies to more complex non-viscometric flows.

[1] Lin NYC, Guy BM, Hermes M, Ness C, Sun J, Poon WCK and Cohen I (2015) *Phys. Rev. Lett.*, 115(22): 228304. [2] Mari R, Seto R, Morris JF and Denn MM (2014) *J. Rheol.*, 58(6): 1693-1724.

Wednesday 3:45 Galleria I

SC36

### **Controlling shear thickening in colloidal dispersions through the addition of nanoclay, polymer, and nonBrownian particles**

Norman J. Wagner, Jacob Lawton, and Maria Katzarova

*University of Delaware, Newark, DE, United States*

Colloidal dispersions exhibit shear thickening and it is often desirable to control the onset and extent of this rheological response through formulation. Controlling particle size, shape, surface interactions, and solvent properties can all be used to systematically and predictively vary the shear thickening behavior of a suspension, but more recently it has been shown that the addition of other particles can dramatically affect the underlying shear thickening of the base colloidal suspension while affecting other aspects of the flow behavior in a qualitatively different manner. In this work, new nanoclay particles are added to a model, well-studied colloidal dispersion and the shear rheology measured with varying nanoclay amount and nanoclay aspect ratio. The results demonstrate that very small additions of nanoclay can dramatically enhance the shear thickening response of the colloidal dispersion. Evidence for depletion interactions in the mixture is observed in the low shear rheology. Measurements suggest the nanoclay may be enhancing the hydrodynamic interactions via confinement of the colloidal dispersion, as has been previously reported for the addition of nonBrownian cubes and spheres to the same colloidal dispersion. (Cwalina et al. JOR 2015, AIChE 2017) Scaling of the shear thickening exponent with confinement supports this viewpoint and provides a method for rational design of dispersions with specific rheological gain. These results are also analyzed within the context of simulations showing the enhancement of hydrodynamic interactions due to confining hard walls by Swan and Brady JFM 2011 as well as by Bian et al. JNNFM 2014.

Wednesday 4:10 Galleria I

SC37

### **First normal stress difference of model attractive colloid polymer depletion mixtures**

Nayoung Park and Jacinta C. Conrad

*Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States*

Non-adsorbing polymers added to colloidal suspensions induce controlled depletion attractions between the particles that modify the particle microstructure. While the effect of interparticle attractions on viscosity is well understood, it is not yet clear how normal stress differences change with attractive interactions. We studied the effect of adding polymers to colloidal suspensions at constant particle volume fraction of  $\phi=0.40$  on the shear rheology, including the first normal stress difference  $N_1$ . We used a new depletion system comprised of poly(2,2,2-trifluoroethyl methacrylate - *co* - *tert*-butyl methacrylate) particles [Kodger et al., *Sci. Rep.* 5, 14635 (2015)] that were refractive index- and density-matched in 80 (w/w)% glycerol in water. Gels induced by adding one of three polyacrylamide depletants (PAM) of differing molecular weight and dispersity (PDI) at similar normalized PAM concentrations in the free volume  $c/c^*$  (where  $c^*$  is the overlap concentration of the polymer) exhibited indistinguishable quiescent microstructure and dynamics. When the PAM  $M_w$  was small, the shear thickening exponent  $\beta$  of the suspension did not change with the addition of PAM up to  $c/c^* = 1.2$ . Correspondingly,  $N_1$  remained negative and only increased slightly with the addition of PAM. In the presence of large polymers, however,  $\beta$  increased slightly, irrespective of the polymer PDI, and  $N_1$  became positive at high shear

rates. Analysis using a friction-based model [Wyart and Cates, *Phys. Rev. Lett.* **112**, 098302 (2014); Guy *et al.*, *Phys. Rev. Lett.* **115**, 088304 (2015); Royer *et al.*, *Phys. Rev. Lett.* **116**, 188301 (2016)] suggested that the presence of large polymers drives the particles to form enough frictional contacts to increase  $N_1$  to positive values. These results suggest that the sign of  $N_1$  can be tuned in colloid + polymer mixtures through the  $M_w$  of the polymer additive.

Wednesday 4:35 Galleria I

SC38

### **Effect of depletion attraction on reversible shear thickening in bimodal silica suspensions in PEG**

Zahra Daneshfar<sup>1</sup>, Fatemeh Goharpey<sup>1</sup>, and Reza Foudazi<sup>2</sup>

<sup>1</sup>*Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Tehran, Iran;*

<sup>2</sup>*Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

Shear thickening in concentrated bimodal suspensions of nanosilica in polyethylene glycol (PEG) is investigated at two size ratio,  $d=3.4$  and  $6.8$  in constant volume fraction  $\phi=0.59$ , below and above the threshold for significant depletion attraction, respectively. The depletion interaction is driven by small particles exclusion from the space between large particles without liquid-liquid phase separation. Experimental results and empirical models for hydrocluster formation showed that the weak attraction between large particles significantly shifts the onset of shear thickening at lower shear rates. Additionally, bimodal suspensions with  $R=0.6$  and  $0.75$  at  $d=6.8$  show reduced zero-shear viscosity compared to bimodal samples with the same  $R$  at  $d=3.4$  size ratio, which can be attributed to the bonding of large particles.

Wednesday 5:00 Galleria I

SC39

### **Rheology and microstructure of semi-dense and dense soft-to-rigid colloidal suspensions in confined flows**

Joao Maia<sup>1</sup>, Shaghayegh Khani<sup>1</sup>, Erika Barcelos<sup>1</sup>, Safa Jamali<sup>2</sup>, and Arman Boromand<sup>3</sup>

<sup>1</sup>*Macromolecular Science and Engineering, Case Western Reserve Univ., Cleveland, OH 44106-7202, United States;*

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Bridging the gap between the micro-structure and rheology, we have investigated the effect of confinement on the shear-thickening behavior of soft to rigid colloidal suspensions in the semi-dense and dense regimes. In a recent numerical study by our group, the role of hydrodynamic lubrication and frictional interactions in rheological response of dense and semi-dense colloidal suspensions was explored and we could successfully replicate the whole range of continuous and discontinuous shear thickening regime, as well as the negative-to-positive first normal-stress difference. Particle-Particle elastic interactions significantly influences the flow behavior and microstructure of such systems and it is expected that this effect will be enhanced in confined geometries. Thus, in this work we report on the rheological behavior and microstructure development of soft to rigid semi-dense and dense colloidal suspensions in Pouseille flow in mildly and strongly confined geometries, and how they are changed from unconfined conditions.

## **Symposium PM**

### **Polymer Melts: From Molecular Rheology to Processing**

Organizers: Reza Foudazi and Richard Graham

Wednesday 1:30 Plaza I

Keynote PM19

### **Unsolved problems in rheology of complex fluids**

Suraj S. Deshmukh

*The Dow Chemical Company, Lake Jackson, TX 77566, United States*

Many products we use everyday like adhesives, thermoplastics, detergents, paints, agrochemicals and cement pastes show complex rheological behavior that is not very well understood. This is because these are highly formulated systems that contain polymers, dispersed solids, flow modifiers, surface active agents, fillers, colorants, solvents etc. Understanding the rheological & interfacial behavior of these complex fluids can be a key factor in determining the application performance and consumer satisfaction with these products. In this talk, I will use primarily videos, images and some of our attempts at rheological characterization of these ubiquitous products. I will also outline our efforts in using a scientific and statistical approach in understanding their rheological behavior as well as strategies used to modify their flow properties to meet the consumer needs. Since, rheological characterization of these systems is fraught with many complications, hence, I will endeavor to outline few of these open-ended flow problems that should pique the curiosity of the rheological community

Wednesday 1:55 Plaza I

PM20

### **Wire melt electrospinning of polymers**

Kai Morikawa<sup>1</sup>, Aniruddh Vashisth<sup>1</sup>, Mohammad Naraghi<sup>1</sup>, and Micah J. Green<sup>2</sup>

<sup>1</sup>*Aerospace Engineering, Texas A&M University, College Station, TX 77840, United States;* <sup>2</sup>*Chemical Engineering, Texas A&M University, College Station, TX 77843, United States*

Polymer fibers are industrially applicable due to their high specific properties. They are used as the building blocks of textiles and fabrics in applications ranging from wearables to reinforcements of composite materials, and liquid/gas filters. These polymer fibers can be processed via a

host of techniques, such as extrusion, dry spinning, wet spinning and electrospinning. Many of these processes result in high micron range diameter fibers. There is a desire to reduce the fiber diameter to increase the specific surface area, while in some cases, reducing the diameter may lead to enhanced performance. Electrospinning can be employed to reduce the fiber diameter to sub-micron ranges. Electrospinning uses a potential difference between a spinneret and collector, and the electrostatic forces thin the polymer down as it travels to the collector. Solution electrospinning is used to fabricate nanometer ranged fibers but the resulting fibers contain residual solvent making them unattractive for some applications. In this work, we utilize melt electrospinning using a wire to concentrate the electric field without using solvents throughout the process. Further, carbon nanotubes are embedded in the polymer to enhance the polarizability and reduce the fiber diameter from the electrostatic forces. We applied this method to process polycaprolactone (PCL). Through this wire electrospinning method, PCL fibers with diameters of 3.7  $\mu\text{m}$  were fabricated. We examined the electrospinning jet in our method with those obtained by other approaches, such as syringe based methods. Our method led to melt electrospun fibers which were ~3-4 times thinner than conventional approaches. The generation of thin fibers is based on the concentrated electrostatic fields that developed around the tip of the wire, as alluded to in our finite element models of the electrostatic field around the wire tip. We also demonstrated the utility of the method to synthesize polyethylene fibers with average diameters of ~10  $\mu\text{m}$ .

Wednesday 2:20 Plaza I

PM21

### **Shear and extensional rheology of entangled bulk polymers functionalized with metal-ligand coordination**

Flanco Zhuge<sup>1</sup>, Salvatore Costanzo<sup>2</sup>, Daniele Parisi<sup>3</sup>, Taisir Shahid<sup>1</sup>, Charles-André Fustin<sup>1</sup>, Jean-François Gohy<sup>1</sup>, Dimitris Vlassopoulos<sup>3</sup>, and Evelyne van Ruymbeke<sup>1</sup>

<sup>1</sup>*Bio and Soft Matter - IMCN, Univeriste catholique de Louvain, Louvain-La-Neuve, Belgium;* <sup>2</sup>*Univ. of Montpellier, Montpellier, France;* <sup>3</sup>*Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece*

The advent of dynamic metal-ligand (M-L) coordination has emerged as a powerful strategy for the design of various self-assembled materials with stimuli-responsive properties. Among them, reversible polymeric networks obtained by functionalizing flexible polymer chains with M-L coordination are a promising avenue to engineer soft materials with tunable mechanical properties. In this work, we investigate the linear, nonlinear shear and uniaxial extensional viscoelasticity of low-polydispersity (below 1.3) entangled poly (n-butyl acrylate) chains functionalized with terpyridine ligands. Upon self-assembly, the telechelic 4-arm star precursors form model networks with minimum fraction of defects. Most of the chain segments participate in the entangled network, contrary to networks originating from linear chains with metal binding ligands along their backbone, which contain a large proportion of dangling chain ends or loops.

These model systems are therefore perfect to investigate how the dynamics of metallo-supramolecular bulk networks (MSBNs) is affected by both the dissociation kinetics of M-L complexes and the disentanglement process, and how these two mechanisms are coupled. The measurements are performed on a filament stretching and on a strain controlled rotational rheometers equipped with a cone-partitioned plate geometry. In extension the MSBNs show strain hardening at extension rates below their respective terminal relaxation times. Since the transient viscosity of MSBNs is measured at low strain rates, the strain hardening is attributed to the physical crosslinks which comprise M-L coordination. On the other hand, strong shear thinning behavior is observed at similar deformation rates in nonlinear shear flow. By altering the temperature, we systematically vary the relative importance of the M-L complexes, which allows us to determine their specific contribution to the network properties. Moreover, the properties of these systems can be finely tailored with varying the ratio or the nature of metal ions.

Wednesday 2:45 Plaza I

PM22

### **Rheological studies of polyacrylonitrile copolymer plasticized with water and ethanol**

Jianger Yu and Donald G. Baird

*Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States*

The melt spinning process of polyacrylonitrile (PAN) has been researched in the past few decades. Compared to the solution spinning process, it does not require toxic organic solvents. The major problem of the PAN melt spinning process is the melting point ( $T_m$ ) of PAN is much higher than its degradation temperature. However, by adding plasticizers, the  $T_m$  of PAN can be significantly reduced. DSC results show water and ethanol based plasticizers can decrease the  $T_m$  of AN/MA copolymer to around 150 degree C, which is 30 degree C below its melting point. Two types of rheological measurements, shear-steady and time-dependent viscosity measurements, have been conducted for the plasticized PAN copolymer as well. All the rheological measurements have been performed in a customized capillary rheometer system with a pressure chamber attached at the end of the rheometer. The entire system is pressurized to 1.38 MPa with nitrogen in order to prevent the plasticizers evaporating and foaming. The pressure is not released until the end of measurements. A capillary with L/D of 73 is used and the entrance effect can be neglected with such a large L/D value. The steady-shear viscosity measurements determined the viscosity of PAN at a shear rates ranging from 10 to 10000  $\text{s}^{-1}$ . (the Rabinowitsch correction was applied to calculate the true wall shear rate) These measurements provided basic rheological data of the PAN copolymer. The time-dependent viscosity measurements tracked the viscosity change at a constant low shear-rate for over 90 minutes. It provided the stability information of the PAN copolymer. The rheological measurements were performed at various temperature from 160 degree C to 190 degree C. These results provide information for determine the feasibility of melt spinning PAN process and basic rheological data for the extruder design.



Wednesday 3:45 Plaza I

PM23

**Decoding the viscoelastic properties of metallo-supramolecular networks moving in a linear polymer matrix**

Evelyne van Ruymbeke and Flanco Zhuge

*Bio and Soft Matter - IMCN, Univeriste catholique de Louvain, Louvain-La-Neuve, Belgium*

Investigating and modelling the viscoelastic properties of binary blends composed of two monodisperse polymers is still, today, a challenge. In particular, this requires taking into account the fact that the long component can relax either by moving in a thin tube representing the influence of all the surrounding entanglements, or by moving in a dilated tube, which only considers the entanglements between the long component, but at the rhythm of the motion of the short chains. This also requires to properly take into account the dynamic tube dilation effect induced by the short chains. In the present work, we first discuss the relaxation of various binary blends, in which the slow component can be linear, star-like or H-like polymer, and is diluted in different short linear matrices. We then extend this study to the relaxation of binary blends composed of metallo-supramolecular star molecules diluted in different linear matrices. By playing with the concentration of supramolecular stars as well as with the molar mass of the linear polymer, we systematically investigate the influence of the short chains motion on the relaxation of the network. We also study the influence of temperature and nature of the metal ions on the lifetime of the transient bonds. The results are then rationalized, based on the TMA tube model that we have recently developed to describe the viscoelastic properties of supramolecular entangled polymers.

Wednesday 4:10 Plaza I

PM24

**Identifying nematic ordering and quantifying its effect on chain entanglement in conjugated polymers**Renxuan Xie<sup>1</sup>, Albree R. Weisen<sup>1</sup>, Enrique D. Gomez<sup>1</sup>, and Ralph H. Colby<sup>2</sup><sup>1</sup>*Chemical Engineering, Pennsylvania State University, University Park, PA 16802, United States;* <sup>2</sup>*Materials Science and Engineering, The Pennsylvania State University, University Park, PA, United States*

The effect of a nematic phase on chain entanglements is probed by linear viscoelastic measurements on poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and poly((9,9-bis(2-octyl)-fluorene-2,7-diyl)-alt-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5'-diyl) (PFTBT) with varying molecular weights. We first verify the existence of nematic phases in both PFTBT and PCDTBT and identify nematic-isotropic transition temperatures, between 260 and 300 °C through a combination of differential scanning calorimetry, polarized optical microscopy, temperature dependent x-ray scattering, and rheology. PCDTBT forms a nematic glass, while PFTBT has a nominal melting temperature  $T_m = 260$  °C. The nematic-isotropic transition temperature depends on the molecular weight, such that the Flory-Fox model predicts the nematic-isotropic transition temperature = 334 °C in the long chain limit for PFTBT. Entanglement molecular weight ( $M_e$ ) in the isotropic phase is extracted to be  $11 \pm 1$  kg/mol for PFTBT and  $22 \pm 2$  kg/mol for PCDTBT by modelling their linear viscoelastic response. Entanglements are significantly reduced through the isotropic to nematic transition, leading to a 10 fold increase in  $M_e$  for PFTBT and a 15 fold increase for PCDTBT in the nematic phase. We propose that reducing entanglements further by aligning the nematic domains through LAOS can promote long range order and enhance charge transport in liquid crystalline conjugated polymers.

Wednesday 4:35 Plaza I

PM25

**Rheology of poly(ethylene-co-methacrylic acid) ionomers: Effects of ionic interactions**Tanja Tomkovic and Savvas G. Hatzikiriakos*Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC V6T-1Z3, Canada*

Using a parallel plate rheometer equipped with a partitioned plate, and an extensional fixture (SER), a full rheological characterization of several commercial ionomers has been carried out including the determination of the linear viscoelastic moduli, the damping function and the tensile stress growth coefficient (extensional viscosity). Particular emphasis has been placed on the effect of ionic association on the rheological behavior, which was studied by comparing the properties of ethylene methacrylic acid copolymer with the corresponding ionomers neutralized with sodium hydroxide. The distribution of the relaxation times to identify the characteristics times such as reptation, Rouse, and sticky-Rouse that is associated with the characteristic life time of the ionic associations has been thoroughly studied. Finally, the experimental rheological data have been fitted to a viscoelastic model (the K-BKZ model).

Wednesday 5:00 Plaza I

PM26

**Use of rheology to understand the influence of compatibilizer structure on the morphology of polymer blends**Nicole R. Demarquette<sup>1</sup>, Julie Genoyer<sup>1</sup>, Marcio Yee<sup>2</sup>, Jeremie Soulestin<sup>3</sup>, and Adriana M. De Souza<sup>2</sup><sup>1</sup>*Génie Mécanique, Ecole de technologie Supérieure, Montreal, Canada;* <sup>2</sup>*Materials Engineering Department, University of Sao Paulo, Sao Paulo, Brazil;* <sup>3</sup>*Ecole des Mines de douai, Douai, France*

Compatibilization of two polymers to form a blend has been used in the industry for many years. It is known to tune and control the morphology of these multiphase materials, which, in turns, controls their engineering properties. However, the influence of compatibilizer structure on the underlying phenomena that govern the role of a compatibilizer as a morphology modifier and stabilizer are not completely understood. For example, it is still unclear when the prevention of coalescence in a droplet dispersion type morphology, brought by the presence of a compatibilizer, originates from steric repulsion of the droplets or from Marangoni stresses induced by redistribution of the compatibilizer during flow. In this work, rheology was used as a tool to understand the different mechanisms of compatibilization for several types of compatibilizers. Block copolymers with different architectures as well as different types of nanoparticules were added to a poly(methyl methacrylate) (PMMA)/polystyrene (PS) blend. The effect of their addition on the blends morphology was studied by scanning and transmission electron microscopy. The different blends were subjected to small amplitude oscillatory shear and stress relaxation tests. Analysing the relaxation spectra of the different blends, it

was possible to understand the mechanisms of compatibilization for the different additives studied. The stress relaxation tests were used to access the stability of morphology when the blends were subjected to flows in the non-linear viscoelastic regime.

## Symposium PG Polyelectrolytes, Self-assembling Systems & Gels

Organizers: Nick Virgilio and Lilian Hsiao

Wednesday 1:30 Bellaire

PG14

### **Extensional relaxation time, pinch-off dynamics and printability of semi-dilute polyelectrolyte solutions**

Leidy N. Jimenez, Jelena Dinic, Ryan Basse, and Vivek Sharma

*Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

Quantitative studies of capillary-driven thinning and pinch-off dynamics of semi-dilute polyelectrolyte solutions, and their response to extensional flows, typically encountered in drop formation applications, are relatively rare, and are the focus of this contribution. Here the pinch-off dynamics and extensional rheology of two model polyelectrolytes: poly (sodium 4-styrenesulfonate) (NaPSS) and poly(acrylic acid) (PAA) in two different solvents are characterized by using dripping-onto-substrate rheometry. Unlike shear relaxation time that decreases with increase in concentration in the unentangled, semi-dilute solutions, the extensional relaxation time of PAA solutions increases with an exponent of  $1/2$ , and entangled solutions also exhibit a stronger concentration dependence of  $3/2$ . In contrast, the extensional relaxation time is not measurable for the unentangled, semi-dilute aqueous NaPSS solutions, though entangled NaPSS solutions show concentration-dependent values. The experiments and analysis described herein elucidate how the interplay of stretching due to electrostatics and hydrodynamics influence extensional rheology response and printability of polyelectrolyte dispersions.

Wednesday 1:55 Bellaire

PG15

### **Effect of polydispersity on the rheological properties of polyelectrolyte solutions**

Aijie Han<sup>1</sup>, Xiuli Li<sup>2</sup>, Louis A. Madsen<sup>2</sup>, and Ralph H. Colby<sup>1</sup>

<sup>1</sup>*Materials Science and Engineering, The Pennsylvania State University, University Park, PA, United States;* <sup>2</sup>*Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, VA 24061, United States*

The relaxation dynamics and conformation of monodisperse polyelectrolyte solutions are well described by the Rouse model and the scaling model in the semidilute unentangled regime. However, many commercial polyelectrolytes have large polydispersity and their shear thinning behaviors are not yet understood. The conventional shear thinning models do not fit the steady shear data of polydisperse polyelectrolytes well due to the polydispersity effects. In this study, we have developed a model to describe the Newtonian viscosity, the recoverable compliance and the longest relaxation time of polydisperse polyelectrolyte solutions based on the Rouse model. Our model has been tested on different commercial polyelectrolytes with unknown polydispersity. The shear rate dependence of viscosity is measured on polyelectrolyte aqueous solutions with varying concentrations from 0.005M to 0.1M. The steady shear rheology is performed over a range of shear rates from  $0.1\text{ s}^{-1}$  to  $800\text{ s}^{-1}$  using strain-controlled rotational rheometers in concentric cylinder geometry. Our model introduces a polydispersity-relevant fitting parameter, showing good agreement with the steady shear data at all concentrations. The Carreau model and the Cross model are also applied, which yield the same values of Newtonian viscosity, but different relaxation times. The Cross model fits the data better than the Carreau model. However, the Cross model gives unreliable estimates of the relaxation time and the power law index due to the lack of high shear rate data in the shear thinning region.

Wednesday 2:20 Bellaire

PG16

### **Influencing liquid crystalline gel formation in cellulose ionic liquid solutions by adding water and nanoparticles**

Ashna Rajeev, Abhijit P. Deshpande, and Madivala G. Basavaraj

*Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India*

Liquid crystalline gels find application in different fields such as, display and storage devices, sensors etc. Recently, it was reported that cellulose dissolved in 1-ethyl-3-methylimidazolium acetate (EmimAc) shows sol-gel transition accompanied by a liquid crystalline phase transition at high cellulose concentrations. In this work we report the preparation of liquid crystalline gel phase from cellulose/ionic liquid solutions by altering the solvent environment due to the addition of water which is an anti-solvent for cellulose. We studied the characteristics of cellulose/ionic liquid/water mixtures at 5 - 15 wt% of cellulose concentrations by combining rheological and polarisation optical microscopy observations. We observed the formation of non-aligned Cholesteric liquid crystalline phase at low cellulose concentration and spherulite-like assemblies at high cellulose concentration. Further we investigated the enhancement of gel properties by incorporating spherical as well as shape anisotropic nanoparticles at different nanoparticle:cellulose weight ratios, into the cellulose/ionic liquid/water gel matrix.

Wednesday 2:45 Bellaire

PG17

**Dynamics of liquid coacervates formed by oppositely charge polyelectrolytes**Christian Aponte-Rivera and Michael Rubinstein*Mechanical Engineering and Materials Science, Duke University, Durham, NC 27710, United States*

Mixtures of oppositely charged polyelectrolytes can undergo phase separation to form a polymer rich phase called a coacervate and a polymer depleted phase. The polymer rich phase can be a soft, viscous liquid, or a solid like complex. Both types have drawn much attention in the literature due to their applications in the food, pharmaceutical, and other industries as well as their role in biological systems. Studies have focused on the formation of the coacervate phase, and models have been developed to predict phase separation and static properties. However, much less attention has been given to predicting the dynamic properties of coacervates, and how these depend on experimentally controllable parameters. We develop a scaling theory for the dynamic behavior of asymmetric liquid-like coacervates formed from oppositely charged polyelectrolyte solutions. Depending on the degree of polymerization, the asymmetric liquid coacervate can form either an interpenetrating double-semidilute structure, wherein both polyanion and polycation are found above their overlap concentration, or a dilute-semidilute structure, where only lower charged polyelectrolytes are found above their overlap concentration. We will discuss a scaling theory for the entangled and unentangled dynamics, providing predictions for the relaxation modulus and steady state shear viscosity of the coacervate, and the diffusivity of the polyelectrolyte chains. The scaling theory will highlight the different dynamical regimes of the system, and how the dynamic properties can be tuned from experimentally controllable parameters such as the degree of polymerization, the number density of charges of the polyanion and polycation, and the strength of electrostatic interactions. The scaling theory provides guidelines for optimizing the dynamic and rheological properties for future applications in the cosmetics, food, and other industries.

Wednesday 3:45 Bellaire

Keynote PG18

**The application of rheology in the development of cosmetic products**Hy Bui*L'Oreal, Clark, NJ, United States*

Cosmetic products can be in anhydrous liquid form (e.g., liquid lipstick or lip gloss), or in oil-in-water (O/W), or water-in-oil (W/O) emulsion form as seen in liquid foundations, skincare products, sunscreen and lotion. In addition, some products are also in gel form (e.g., hair styling gel or foundation gels). The cosmetic formulations contain many ingredients including polymers, surfactants, oils, water, pigments and preservatives. Interactions between these ingredients play an important role in influencing stability, texture, performance and sensory characteristics of the final products. Therefore, rheology is employed during various stages of product development, starting from the proof of technical concept to the sensory evaluations, in addition to addressing stability issues and other scale-up issues during manufacturing. This talk will focus on the challenges in cosmetic science and the application of rheology to the field, illustrated through some examples in make-up and skin care.

Wednesday 4:10 Bellaire

PG19

**Structure and rheology of polypeptide complex coacervates**Samanvaya Srivastava<sup>1</sup>, Amanda Marciel<sup>2</sup>, and Matthew V. Tirrell<sup>2</sup><sup>1</sup>*Chemical and Biomolecular Engineering, University of California Los Angeles, Los Angeles, CA 90095, United States;* <sup>2</sup>*IME, University of Chicago, Chicago, IL 60637, United States*

Scattering investigations of the structure and chain conformations and the rheological properties of polyelectrolyte complexes (PECs) comprising model polyelectrolytes are presented. The use of charged polypeptides - (poly)-L-lysine and (poly)-(L,D)-glutamic acid with identical backbones allowed for facile tuning of the system parameters, including chain length, side-chain functionality, and chirality. Systematic studies using small-angle X-ray scattering (SAXS) of liquid PEC coacervates revealed a physical description of these materials as strongly screened semidilute polyelectrolyte solutions comprising oppositely charged chains. At the same time, solid PECs were found to be composed of hydrogen-bonding driven stiff ladder-like structures. While the coacervates behaved akin to semidilute polyelectrolyte solutions upon addition of salt, the solids were largely unaffected by it. Rheology measurements of PEC coacervates revealed a terminal relaxation regime, with an unusual plateauing of the storage modulus at low oscillation frequencies. The plateau may be ascribed to a combination of instrumental limitations and the long-range electrostatic interactions contributing to weak energy storage modes. Excellent superposition of the dynamic moduli was achieved by a time-salt superposition. The shift factors, however, varied more strongly than previously reported with added salt concentration.

Wednesday 4:35 Bellaire

PG20

**The role of extensional kinematic flow field in the study of supramolecular stress recovery**Zachary R. Hinton<sup>1</sup>, Aamir Shabbir<sup>2</sup>, and Nicolas J. Alvarez<sup>1</sup><sup>1</sup>*Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States;* <sup>2</sup>*Coloplast, Hulebaek, Denmark*

Polymers with intrinsic self-healing ability are a broadening class of materials with useful applications from medical devices to industrial adhesives. Rheological quantification of these materials is seriously lacking in the literature leading to very little quantification and fundamental understanding of the recovery phenomena and resulting rheology. In this work we use model supramolecular networks consisting of poly-(n-butyl acrylate) (PnBA), poly-(acrylic acid) (PAA), poly-(methoxyethyl acrylate) (PMEA) and 2-ureido-4[1H]-pyrimidinone bearing methacrylate (UPyMA) to explore the complex dynamics of self-healing. We show the importance of the kinematic flow field on the measured degree of stress recovery. The degree of recovery is strongly dependent on the rate of extension, the applied stress, and the relaxation time of the polymer network.

We also show that there are two governing timescales for the degree of stress recovery: the time between fracture and adhesion and the relaxation time after adhesion. This work shows that recovery is a sequential processes wherein reptation is followed by re-association.

## Symposium SG Solids, Composites & Granular Materials

Organizers: Jonathan Seppala and Denis Rodrigue

Wednesday 1:30 Post Oak

SG6

### **Unveiling the effects of heterogeneity and sub-entanglement chain stretching on the mechanical response of deformed polymeric glass**

Weizhong Zou<sup>1</sup>, Soroush Moghadam<sup>2</sup>, Robert S. Hoy<sup>3</sup>, and Ronald G. Larson<sup>4</sup>

<sup>1</sup>University of Michigan, Ann Arbor, MI, United States; <sup>2</sup>Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI, United States; <sup>3</sup>Department of Physics, University of South Florida, Tampa, FL 33620, United States; <sup>4</sup>Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States

We present a coarse-grained picture of polymeric glass that divides the stress into a series of distinct segmental modes governing the monomer friction, and a polymer mode contributed by the configuration of polymer chains. In this hybrid model, the discrete relaxation time spectrum of individual segmental modes is derived by fitting the KWW function whose time constant and non-exponentiality are obtained from dye reorientation experiments (Lee, et al. J. Polym. Sci. B, 47, 1713, 2009; Bending & Ediger J. Polym. Sci. B, 54, 1957, 2016); while the polymer mode is represented by finitely extensible bead-spring chains whose conformational changes are solved by Brownian dynamics simulation with the bead drag coefficient proportional to the averaged viscosity of segmental modes. The model is shown to successfully reproduce both the pre-yielding and the post-yielding behaviors of PMMA (poly-methymethacrylate) glass under constant rate of extension and uniaxial tensile creep. The obtained parameters, such as predeformation aging time, rubbery and shear modulus, are all in good agreement with the properties of the glass and its preparation history. When compared to molecular dynamics simulations for entangled Kremer-Grest chains under uniaxial extension, the conformation of chains predicted from both MD and BD simulations turn out to be very similar at large deformation (1.8 Hencky strain) where strain hardening arises and individual molecules start to collapse into folded states (so-called kinks), analogous to that in fast extensional flows of dilute polymer chains. We show from the MD simulations that very few of the folds are entangled with other chains, and so the above similarity provides strong evidence that the high tensions in those folded sub-entangled polymer strands is the cause of the strain hardening rather than the deformation of entanglement networks.

Wednesday 1:55 Post Oak

SG7

### **Structure-property relation in polymer glasses: Correlation between deformation kinetics and molecular structure**

Coen Clarijs<sup>1</sup>, Vito Leo<sup>2</sup>, and Leon Govaert<sup>1</sup>

<sup>1</sup>Mechanical Engineering, Polymer Technology, Eindhoven University of Technology, Eindhoven 5612AP, The Netherlands;

<sup>2</sup>Solvay Specialty Polymers, Brussels, Belgium

The deformation kinetics of polymer glasses can be accurately described by Eyring's activated flow theory. Important parameter in the theory is the Eyring activation volume, often stated to be of the order of the unit of flow in the polymer. Many attempts have been made in the past trying to relate the activation volume to molecular structure, however comparing it to for example repeat unit or Kuhn segment volume does not yield a satisfactory correlation. An interesting series of papers on chain dimensions was presented by Lewis Fetters and co-workers, discussing the role of the so-called packing length on polymer melt viscoelastic properties. The packing length is defined as the ratio of the occupied volume of a polymer coil to its pervaded volume. It was shown that a unique relation exists between the packing length and the molecular weight between entanglements.

In this study we investigate a correlation between the rate dependence of the yield stress, reflected in the Eyring activation volume, and molecular structure, reflected in the packing length. Experimental data on more than 20 polymer glasses were collected, obtained from experiments performed in our laboratories over the past decades. Packing lengths are taken from the work of Fetters et al., or if unavailable, calculated from reported or measured plateau moduli. From the results it is observed that a strong correlation exists. With an increase in packing length the activation volume decreases, i.e. a stronger dependence of the yield stress on strain rate. The packing length can be likened to the chain thickness, and indeed bulkier polymers like for example polystyrene display high values of the packing length, but low activation volumes.

Wednesday 2:20 Post Oak

SG8

### **Rheological behavior of polypropylene reinforced with cellulose filaments**

Julie Genoyer<sup>1</sup>, Nicole R. Demarquette<sup>1</sup>, Helen Lentzakis<sup>2</sup>, and Abdou Khadri Diallo<sup>2</sup>

<sup>1</sup>Génie Mécanique, Ecole de Technologie Supérieure, Montreal, Canada; <sup>2</sup>Kruger Biomatériaux Inc., Montreal, Canada

Cellulose is the most abundant natural polymer on Earth. It is a biodegradable macromolecule with a semi-crystalline structure that can be extracted from plants, some marine animals and bacteria. Cellulose filaments (CF), mechanically obtained from kraft fibers, are unique filaments with a high aspect ratio which gives them notable mechanical and rheological properties that enable their use as rheology modifiers, mechanical

reinforcement additives when incorporated in several materials such as paper, thermoplastics, thermosets and concrete. Particularly, it was shown by numerous publications that their addition to polymers, at relatively low loading levels, resulted in a good improvement of the mechanical properties of the material while maintaining good flow properties and low density which makes them suitable candidates for new eco-friendly nanocomposites. However, to our knowledge, the rheological behavior of cellulose filaments nanocomposites is rarely studied and is quite unknown. In this work, polypropylene (PP) reinforced with CF was studied. Nanocomposites with CF loadings ranging from 0 to 30 wt% were extruded and characterized. The mechanical properties of those samples showed an improvement in the rigidity and strength of the material. Their rheological properties were evaluated by carrying out small amplitude oscillatory shear tests, showing a significant increase in the storage modulus at low frequency due to the reinforcement of the resin by the fibers after a certain percolation threshold. Rheological results were in agreement with the mechanical properties of the materials and the dispersion state of CF, allowing us to use rheology as a tool to evaluate the dispersion of CF in a polymer.

Wednesday 2:45 Post Oak

SG9

### **Studies on single-screw extrusion of wood-polymer composites with slip effects**

Krzysztof Wilczynski, Kamila Buziak, Adrian Lewandowski, and Andrzej Nastaj

*Department of Polymer Processing, Warsaw University of Technology, Warsaw 02-524, Poland*

Extensive experimental and theoretical studies on rheology and processing of wood-polymer composites have been performed. These are very limited in the literature [1]. Slip effects have been investigated numerically for single screw extrusion using Ansys-Polyflow software. Fully three-dimensional non-Newtonian analysis has been performed both in the extruder (on the screw and barrel surfaces) and in the die. The power-law model of Ostwald-de Waele has been used for the flow modeling and the generalized law of Navier has been applied for the slip analysis. Screw pumping characteristics and die characteristics (i.e. flow rate vs. pressure gradient characteristics) have been developed and then implemented into the recently developed (at the Warsaw University of Technology) global model of the single screw extrusion process of wood-polymer composites [2]. This model makes it possible to predict material flow rate (extrusion throughput), pressure and temperature profiles, material melting profile and power consumption. Rheological equation of Klein has been used in the model for the flow modeling. Rheological characteristics of the wood-polymer composites have been investigated using high pressure capillary rheometry. Slipping has been studied using Mooney approach. Process simulations have been performed and validated experimentally for the polypropylene (PP) based composites of different wood flour (WF) content. The effect of slipping on single screw extruder operation, i.e. location of the operating point on the screw-die characteristics has been discussed.

[1] K.Wilczynski, A.Nastaj, A.Lewandowski, K.J.Wilczynski, K.Buziak, *Int. Polym. Proc.* 2015, v.30, p.114-120; [2] K.Wilczynski, K.Buziak, K.J.Wilczynski, A.Lewandowski, A.Nastaj, *Polymers* 2018, 10, 295; doi:10.3390/polym10030295

Acknowledgments: The authors would like to acknowledge support from National Science Center, Poland (DEC-2015/19/B/ST8/00948).

Wednesday 3:45 Post Oak

SG10

### **Stimuli-responsive soft composites with semiflexible polymers**

Gaurav Chaudhary<sup>1</sup>, Jin Gu Kang<sup>2</sup>, Ashesh Ghosh<sup>2</sup>, N Ashwin K. Bharadwaj<sup>3</sup>, Kenneth Schweizer<sup>2</sup>, Paul V. Braun<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup>

<sup>1</sup>*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>3</sup>*Nike Inc, Portland, OR, United States*

We fabricate two soft composite systems capable of unprecedented change in their mechanical properties in response to magnetic and thermal excitation. The composites were formed by integrating stimuli-responsive particles: micron sized magnetically active iron particles, and highly swollen temperature-responsive Poly(N-isopropylacrylamide) microgels, each integrated into the stiffening network of biopolymer fibrin. We hypothesize that the interaction between the stimuli-responsive particles and fibrin mesh induces local tensile stresses in the fibrin mesh, which inherently stiffens under the stress owing to its semi-flexible nature. This helps achieve a higher sensitivity to the external field in the fabricated composites compared to the traditional flexible-polymer matrix of composite systems. Our approach of using composites based on semi-flexible polymers with strong inherent nonlinearity offers a promising method for developing functional materials with actively tunable mechanical properties.

Wednesday 4:10 Post Oak

SG11

### **Electrically conductive graphene/polyolefin nanocomposites**

Muhammad Z. Iqbal<sup>1</sup> and Matthew W. Liberatore<sup>2</sup>

<sup>1</sup>*Chemical and Petroleum Engineering, United Arab Emirates University, Al Ain, Abu Dhabi 15551, United Arab Emirates;*

<sup>2</sup>*Chemical Engineering, University of Toledo, Toledo, OH 43606, United States*

A unique combination of excellent electrical, thermal, and mechanical properties enable graphene as a multi-functional reinforcement for polymer nanocomposites. However, poor dispersion of graphene in non-polar polyolefins limits its applications as a universal filler. In this presentation, we discuss our research on improving the dispersion of graphene in polyolefins to produce electrically conductive nanocomposites. Highly non-polar nature of polyethylene (PE) was altered by blending it with a polar polymer, called oxidized polyethylene (OPE). Blends of PE with OPE were synthesized via solution blending method. The inclusion of OPE in PE produced miscible blends, but the miscibility decreased with increasing OPE load-ing. Meanwhile, Young's modulus of blends increased with increasing OPE con-centration, attributed to decreased long

period order in PE and increased crystallinity. In addition, the miscibility of OPE in PE substantially reduced the viscosity of blends. Electrically conductive nanocomposites were manufactured by incorporating graphene in PE/OPE blends via solution blending. The rheological and electrical percolations decreased substantially to 0.3 and 0.13 vol% in blend/graphene nanocomposites compared to 1.0 and 0.3 vol% in PE/graphene nanocomposites. Improved dispersion of graphene in blends was attributed to increased graphene/polymer interactions, leading to a high aspect ratio of the dispersed graphene. A universal Brownian dispersion mechanism for graphene was concluded similar to that of carbon nanotubes, following the Doi-Edwards theory. Furthermore, the improved dispersion of graphene correlated with the formation of surface fractals in blend/graphene nanocomposites, whereas the poor dispersion of graphene in PE led to the formation of only mass fractals.

Wednesday 4:35 Post Oak

SG12

### **Rheological optimization of hydroxyl grafted polybutadiene/clay nanocomposites**

Vijesh A. Tanna<sup>1</sup>, Joshua Enokida<sup>1</sup>, E. Bryan Coughlin<sup>1</sup>, and H. Henning Winter<sup>2</sup>

<sup>1</sup>*Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States;* <sup>2</sup>*Chemical Engineering, Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

Exfoliating clay in a polymer matrix has been known to be a time and energy intensive process, except for “self-exfoliation”, which occurs to clay when suspended in a hydroxyl terminated polybutadiene. With minimal energy input, the clay can be exfoliated and form a soft solid (physical gel). Beyond hydroxyl termination of polybutadiene, little is known about the properties that prepare the polymer matrix for successful self-exfoliation. To address this deficiency, a series of polybutadienes were synthesized with increasing density of hydroxyl end groups, by grafting mercaptoethanol to the polybutadiene backbone. The hydroxyl grafts increased the polymer's glass transition and viscoelastic properties. With this understanding, a range of polymer nanocomposites were fabricated and it was found that composites comprised of high hydroxyl concentration exhibited lower viscoelastic properties. These findings suggest for the two-step exfoliation process that (1) intercalation is governed by concentration of functional end-groups and (2) exfoliation can only be achieved when the polymer's mobility is high enough.

Wednesday 5:00 Post Oak

SG13

### **The time-temperature superposition principle in polymer nanocomposites**

Shiwang Cheng

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The time-temperature superposition (TTS) principle is often applied to construct the master curves of linear viscoelastic moduli of polymer nanocomposites (PNCs)[1, 2], although the concerns on the validation of the TTS in PNCs have been raised for long [3]. The confusion is largely due to a lack of the methodology that can directly probe the chain relaxation in PNCs of high nanoparticle loadings. In this work, we aim to examine the validation of the TTS through a combination of dielectric spectroscopy and rheology. Dielectric measurements show the similar temperature dependence of the chain relaxation as the alpha relaxation, which strongly deviates from the shifting factor obtained from rheology with only horizontal shifts. Our results indicate strongly the failure of TTS in PNCs, especially PNCs with high loadings of nanoparticles, and strong caution needs to be paid when discussing the master curves of linear viscoelastic moduli of polymer nanocomposites (PNCs). Moreover, discussions of the possible reasons for the failure of TTS in PNCs has also been included.

[1]Baeza, G. P.; Dessi, C.; Costanzo, S.; Zhao, D.; Gong, S.; Alegria, A.; Colby, R. H.; Rubinstein, M.; Vlassopoulos, D.; Kumar, S. K., *Nat. Commun.* 2016, 7, 11368. [2] Mujtaba, A.; Keller, M.; Ilich, S.; Radosch, H. J.; Beiner, M.; Thurn-Albrecht, T.; Saalwächter, K., *ACS Macro Letters* 2014, 3 (5), 481-485. [3] Berriot, J.; Montes, H.; Lequeux, F.; Long, D.; Sotta, P., *Macromolecules* 2002, 35 (26), 9756-9762.

## **Symposium ET Advanced Experimental Techniques/Methods in Rheology**

Organizers: Kalman Migler and Simon Rogers

Wednesday 1:30 San Felipe Room

ET19

### **Inferring dynamic moduli from stress relaxation in aging materials**

Sachin Shanbhag<sup>1</sup>, Yogesh M. Joshi<sup>2</sup>, and Asheesh Shukla<sup>2</sup>

<sup>1</sup>*Scientific Computing, Florida State University, Tallahassee, FL 32306, United States;* <sup>2</sup>*Chemical Engineering, Indian Institute of Technology, Kanpur, Kanpur, India*

We use an aqueous suspension of Laponite, which is a model aging soft glassy material to address the challenging problem of obtaining dynamic moduli from relaxation modulus for a time-dependent material. The effect of aging is suppressed by transforming the experimentally obtained relaxation modulus from the real-time domain to the effective-time domain by normalizing real-time with a time-dependent relaxation time. The relaxation modulus in the effective-time domain is then used to predict the dynamic moduli in the frequency domain. The predictions agree with the shape of the experimental dynamic moduli, but are offset by a factor of about two. Careful analysis reveals that contamination of slow aging modes by fast non-aging modes is responsible for the discrepancy. When this factor is accounted for, quantitative agreement between predicted and experimental data is achieved. This study offers guidelines for generalizing the principles of linear viscoelasticity to time-dependent materials.

Wednesday 1:55 San Felipe Room

ET20

**Study of the rheological behavior of molten polyethylene and numerical simulation of flow in OpenFoam**André M. Castro<sup>1</sup>, Juliana O. Pereira<sup>2</sup>, Argimiro R. Secchi<sup>2</sup>, and Verônica M. Calado<sup>1</sup><sup>1</sup>*Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil;* <sup>2</sup>*Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil*

Determining the most appropriate model and its set of parameters to describe the rheological behavior of a given viscoelastic fluid under actual processing conditions remains a challenging subject in the field of polymer rheology. During extrusion and injection operations the polymer at high temperature is subjected to high rates of deformation, causing orientation and elongation of the chains. In this work, a linear low-density polyethylene sample was used to obtain molten characteristics under processing conditions. TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetry) analysis were performed on the sample to determine in which temperature the tests should be carried out. A MultiPass Rheometer with optical module was used for the acquisition of flow-induced birefringence images of the sample at 140°C through slit-die geometry with 1.5 mm length. The bright and dark fringe patterns observed in these images were related to the stress field during the flow. In the region of constant pressure drop, the principal stress difference (PSD) module profile was determined along the flow centerline for three flow speeds with the GIMP open-source software. These data, associate with small amplitude oscillatory shear (SAOS) experiment obtained in a rotational rheometer, were used to estimate the relaxation spectrum and nonlinear parameters of the constitutive model. Two-dimensional flow simulations using the Giesekus model with four relaxation modes were performed in the viscoelasticFluidFoam solver available on the OpenFOAM software for computational fluid dynamics (CFD). A computational mesh with 81000 hexahedral finite volumes and symmetry condition was employed to represent the slit-die geometry used in the experiment. The results showed that the chosen constitutive model and 4 Maxwell modes were able to describe the viscoelastic fluid behavior under these flow conditions and to reproduce the experimental observations in the multipass rheometer.

Wednesday 2:20 San Felipe Room

ET21

**Computing the linear viscoelastic properties of soft gels using an Optimally Windowed Chirp protocol**Mehdi Bouzid<sup>1</sup>, Bavand Keshavarz<sup>2</sup>, Michela Geri<sup>2</sup>, Thibaut Divoux<sup>3</sup>, Emanuela Del Gado<sup>4</sup>, and Gareth H. McKinley<sup>2</sup><sup>1</sup>*LPTMS, Université Paris Sud, Paris, France;* <sup>2</sup>*Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States;* <sup>3</sup>*MSE2, CNRS Bordeaux, CNRS-MIT, Cambridge, MA, United States;* <sup>4</sup>*Georgetown University, Washington, DC, United States*

We use molecular dynamics simulations of a model three-dimensional particulate gel, to investigate the linear viscoelastic response. The numerical simulations are combined with a novel test protocol (the optimally-windowed chirp or OWCh), in which a continuous exponentially-varying frequency sweep windowed by a tapered cosine function is applied. The mechanical response of the gel is then analyzed in the Fourier domain. We show that i) OWCh leads to an accurate computation of the full frequency spectrum at a rate significantly faster than with the traditional discrete frequency sweeps, and with a reasonably high signal-to-noise ratio, and ii) the bulk viscoelastic response of the microscopic model can be described in terms of a simple mesoscopic constitutive model. The simulated gel response is in fact well described by a mechanical model corresponding to a fractional Kelvin-Voigt model with a single Scott-Blair (or springpot) element and a spring in parallel. By varying the viscous damping and the particle mass used in the microscopic simulations over a wide range of values, we demonstrate the existence of a single master curve for the frequency dependence of the viscoelastic response of the gel that is fully predicted by the constitutive model. By developing a fast and robust protocol for evaluating the linear viscoelastic spectrum of these soft solids, we open the path towards novel multiscale insight into the rheological response for such complex materials.

Wednesday 2:45 San Felipe Room

ET22

**Time-strain separability in medium-amplitude oscillatory shear (MAOS)**

Luca Martinetti and Randy H. Ewoldt

*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

For a time-strain separable (TSS) model, what is the value of weakly-nonlinear medium-amplitude oscillatory shear? MAOS only probes leading-order nonlinearities, thus involving only one fitting parameter beyond linear viscoelasticity. Yet, we will show that a TSS MAOS response determines more than just that nonlinear parameter. In particular, it significantly improves inference of the terminal distribution of relaxation times, relative to small-amplitude oscillatory shear for the same range of frequency. We will also show the first examples of non-liquid-like terminal MAOS response. This will be accomplished by considering the Coleman-Noll class of “third-order simple materials” (both liquids and solids), with arbitrary linear memory function, and deriving TSS MAOS equations that are uniquely determined by linear viscoelastic behavior. Examples of the latter will include the Doi-Edwards model (showing the MAOS response with and without the independent alignment approximation), and the Maxwell and Zener models (both classical and fractional versions).

Wednesday 3:45 San Felipe Room

ET23

**The effect of instrumental inertia on large amplitude oscillatory shear (LAOS) testing of starch suspensions**Merve Yildirim<sup>1</sup>, Hazal Turasan<sup>2</sup>, and Jozef Kokini<sup>1</sup><sup>1</sup>Food Science, Purdue University, West Lafayette, IN 47907, United States; <sup>2</sup>Purdue University, West Lafayette, IN 47907, United States

Starch suspensions are known to be shear thickening at higher concentrations due to the formation of hydroclusters bonded with hydrodynamic lubrication forces. The determination of non-linear properties of starch suspensions using large amplitude oscillatory shear (LAOS) can help in offering insights on improving the design of flow processes such as mixers and can lead to better quality products. In this study starch suspension using starches with different amylose/amylopectin ratios at concentrations of 48, 49, 50, 51, 52% were studied in the strain range of 0.01-500% at a frequency of 10 rad/s using the concentric cylinder geometry of DHR-3 rheometer. Starch suspensions were prepared with deionized water and carboxymethylcellulose (CMC) in order to inhibit suspension settling. The raw stress responses in the non-linear region were evaluated with Fourier transformation available through TRIOS and non-linear rheological properties were obtained as a function of strain. The raw stress response curves of starch suspensions between the shear thinning and shear thickening regions have uncommon beating patterns, where the instrumental inertia exceeds the limits. The limits of instrumental inertia were evaluated by both raw phase angle and torque ratio which is the ratio of instrumental inertia to sample torque. We observed that as the concentration of starch increased the onset amplitude from linear to the nonlinear region increased. The instrumental inertia effect decreases as the solid volume ratio increased and as the concentration of CMC increases added into suspension increased, instrumental inertia decreased. We have improved our analysis by focusing on the region where inertia is acceptably small. This analysis and these results will be presented and limitations will be discussed.

Wednesday 4:10 San Felipe Room

ET24

**Making MAOS faster, better, and more insightful**Piyush K. Singh<sup>1</sup>, Luca Martinetti<sup>1</sup>, Tiffany R. Price<sup>1</sup>, Johannes M. Soulages<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup><sup>1</sup>Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States; <sup>2</sup>Corporate Strategic Research, ExxonMobil Research and Engineering, Annandale, NJ 08801, United States

We describe our recent advances in experimental and model fitting methods for intrinsically-nonlinear medium-amplitude oscillatory shear (MAOS) rheology [1]. This includes: (A) frequency-sweep techniques for faster data acquisition [2], (B) model fitting with proper weighting based on data uncertainty [3], and (C) model selection guided by Bayesian information criteria (BIC) using multimode and continuous viscoelastic spectra in nonlinear models. Methods are demonstrated with polymer melts including a linear & well-entangled cis-1,4-polyisoprene system. Multiple constitutive models are compared by fitting to the full data set, which is more reasonable with the intrinsically-nonlinear MAOS considered here compared to the higher-dimensional large-amplitude oscillatory shear (LAOS). Models considered include Giesekus and the time-strain separable memory integral, each with varying numbers of modes and several different functional forms to describe a continuous relaxation spectrum. Our work demonstrates how the low-dimensionality of MAOS is a benefit in terms of faster data acquisition, better data confidence, and meaningful fitting of constitutive models which allows for molecular and microstructural inference.

[1] Ewoldt, R.H., & N.A. Bharadwaj, "Low-dimensional intrinsic material functions for nonlinear viscoelasticity," *Rheol. Acta* 52, 201-219 (2013); [2] Singh, P.K., J. M. Soulages, & R.H. Ewoldt, "Frequency-sweep medium-amplitude oscillatory shear (MAOS)," *J. Rheol.* 62(1), 277-293 (2018); [3] Singh, P.K., J. M. Soulages, & R.H. Ewoldt, "On fitting data for parameter estimates: residual weighting and data representation," submitted.

Wednesday 4:35 San Felipe Room

ET25

**Influence of experimental setup on squeeze flow behavior of mortars as measured by dynamic pressure mapping**Fábio A. Cardoso, Franco A. Grandes, Andressa A. Rego, and Rafael G. Pileggi*Department of Construction Engineering - Escola Politécnica, University of São Paulo, São Paulo, São Paulo 05508-070, Brazil*

Squeeze flow is a rheological test based on the compression of a sample between parallel plates and is used as alternative/complementary method for characterizing fresh mortars. Its geometry change makes the technique particularly interesting, as it creates flow conditions similar to those involved in processing and application of mortars (pumping, spraying, spreading, extrusion). As a result, a testing method for rendering and masonry mortars was standardized in Brazil (ABNT NBR 15839:2010). Up to date, methods assume that stress under the plate evolves uniformly; however, stress distribution may not behave as expected, either because of phase separation or by the presence of macroscopic particles. Different test setups may be used, which change edge effects and sample geometry. In a constant volume condition, the whole sample is continuously loaded as its area increases; with constant area configuration, on the other hand, part of the material flows out of the plates. The ratio between initial height and radius may affect flow regime. In this work, the influence of the experimental setup and phase segregation are investigated by the association of squeeze flow and a pressure mapping system. Two displacement rates (0.1 and 3.0 mm/s) and three setups are employed: constant area with initial sample diameter of 101 mm (CA100); constant area with initial sample diameter of 50.5 mm (CA50); and constant volume with initial sample diameter of 50.5 mm (CV50). Liquid phase migration was quantified to support the analysis. Two compositions of rendering cement mortars were analyzed, with and without a viscosity modifying cellulose ether based admixture. The mean pressure evolution was roughly the same independent of test setup for the materials in the conditions explored. The pressure mapped squeeze flow (PMSF) method provides new information to complement the rheological evaluation of mortars. For the constant volume setup, the evolution of the measured area collaborates to assess material compressibility phenomena.



Wednesday 5:00 San Felipe Room

ET26

**Rheo-kinetic study of thermoplastic polyurethane synthesis using in situ Rheo-FTIR analysis**Joao Maia<sup>1</sup>, Dana Klein<sup>1</sup>, Arman Boromand<sup>2</sup>, and Jesse Gadley<sup>1</sup><sup>1</sup>Macromolecular Science and Engineering, Case Western Reserve Univ., Cleveland, OH 44106-7202, United States;<sup>2</sup>Department of Mechanical Engineering & Materials Science, Yale University, New Haven, CT 06520-8286, United States

Thermoplastic polyurethanes (TPUs) are widely used materials, but little is known about the kinetics of thermoplastic polyurethanes (TPUs) synthesized under flow, despite the dependence of their properties on the processing conditions they were subjected to during synthesis. This study makes use of a novel instrument to simultaneously collect in situ FTIR (direct) measurements and rheological (indirect) measurements to better understand the kinetics of TPU forming reactions. For TPUs with different amounts of hard segment, produced under quasi-quiescent (minimal shear) conditions, distinct differences in the reaction rate were observed. Increasing the shear rate imposed on a single model TPU composition confirmed that the system is sensitive to its flow environment and, in fact, a positive linear correlation between the applied shear rate and the reaction rate was found. The combination of IR and rheological measurements enabled the development of a simple phenomenological model that enables the viscosity achieved by a system of a specific conversion to be estimated and vice versa.

### Symposium FE Foams, Emulsions & Interfacial Rheology

Organizers: John Frostad and Joseph Samaniuk

Wednesday 1:30 Tanglewood

FE10

**Atypical, non-cubical of asymptotically nonlinear viscoelasticity power law scalings of capillary suspensions**Irene Natalia<sup>1</sup>, Randy H. Ewoldt<sup>2</sup>, and Erin Koos<sup>1</sup><sup>1</sup>Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium; <sup>2</sup>Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

Most studies on the leading order of asymptotically nonlinear response reported a cubical scaling  $\sigma \propto O(\dot{\gamma}^3)$  as explained by memory-integral expansion [1]. Here, we report atypical, non-integer medium-amplitude oscillatory shear (MAOS) power law scaling for capillary suspensions, i.e. particle suspensions in a two-fluid system with capillary interactions. Furthermore, as never been reported before, we observed different power law exponents for the storage and loss moduli. This phenomenon is valid across a range of different capillary suspension compositions. Our experimental work constitutes the strongest evidence yet that non-integer scalings exist and provides insights into their cause.

The MAOS scaling often correlates with the microstructure. The addition of a small amount of secondary fluid that is immiscible to the bulk fluid induces a strong attractive capillary force between the particles and two fluids which results in a sample-spanning network. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles and a capillary state when the bulk fluid is preferentially wetting.

The capillary bridges rupture under shear and then rebuild the network upon cessation. Such thixotropic behavior might be the origin of the atypical scaling, as has been observed from a Carbopol system by Blackwell and Ewoldt [3]. While their thixotropic-viscoelastic model predicted a non-integer scaling, it did not predict distinct exponents for the storage and loss moduli, as observed in our capillary suspensions. This discrepancy might arise because of the heterogeneous, fractal microstructure in the percolated sample-spanning network or due to a violation of the simple potential field. The influence of the relative secondary fluid volume will also be discussed for both capillary and pendular states.

[1] Davis, Macosko, JoR, 1978; [2] Koos, Willenbacher, Science, 2011; [3] Blackwell, Ewoldt, JNFM, 2016.

Wednesday 1:55 Tanglewood

FE11

**Role of interfacial viscosity and bending resistance on droplet deformation, translation, rheology, and breakup**Vivek Narsimhan

Chemical Engineering, Purdue University, West Lafayette, IN 47907, United States

There is a lot of interest in characterizing the mechanics of droplet-like systems with interfaces that cannot be solely described by surface tension. Some examples include red blood cells, vesicles, pickering emulsions, and asphaltenes. In this talk, we discuss some of our recent work on such systems. The first part of the talk discusses droplets with a thin layer of viscous, insoluble surfactant whose mechanics are described by interfacial viscosity, i.e., a Boussinesq-Scriven constitutive law. We develop analytical theories to quantify droplet shape under flow in the limit of weak deformation, to a sufficient level of approximation where one can extract information about non-linear rheology and droplet breakup. In shear flow and extensional flows, we calculate how interfacial viscosity alters the extra stress of a dilute suspension of droplets, in particular the shear stress, extensional stress, normal and stress differences. Other areas quantified include droplet breakup, translation, and particle lift. For droplet translation, we find that surface shear viscosity does not modify the translational speed, which can be explained using simple symmetry arguments. In the last part of the talk, we present some experimental and simulation results on another droplet-like system with a complex interface -- giant unilamellar vesicles, i.e., droplets of ~20 microns with a phospholipid bilayer that exhibits dilatational and bending resistance. We show that the mechanical stability of these systems depend intimately on flow type and flow history, and that the presence of a phospholipid membrane gives rise to dynamical shapes that are very different than that of a clean droplet. In particular, we present some preliminary results quantifying vesicle shape transitions in mixed, linear flows.

Wednesday 2:20 Tanglewood

FE12

**Interfacial viscoelasticity - the effect of polymer chain flexibility and hydrophobicity**Daniel Ashkenazi and Moshe Gottlieb*Chemical Engineering, Ben Gurion University, Beer Sheva 8410501, Israel*

The relationship between the phase behavior of polymer monolayers as studied by the classical rectangular Langmuir-Pockels trough, the rheological properties of the interface, and the importance of the detailed test geometry were recently described and analyzed in detail<sup>1</sup>. Based on this analysis we study in this contribution the behavior of monolayers formed on the water/air interface by several distinctly different polymers: glassy vs. a highly flexible, and hydrophobic (poor solvent at 2d) vs. somewhat hydrophilic (good solvent at 2d). The effect of deformation rates (De number) and relaxation behavior as exhibited by the polymer in the surface pressure-area experiments is contrasted with rheological data and interfacial organization. Highly different behavior is observed when comparing the different polymers.

1. M. Pepicelli, T. Verwijlen, T.A. Tervoort, and J. Vermant "Characterization and modelling of Langmuir interfaces with finite elasticity" *Soft Matter* 2017, 13, 5977-5990.

Wednesday 2:45 Tanglewood

FE13

**Interfacial viscoelasticity of the native oxide layer on gallium based liquid metal alloys**Alan R. Jacob, Dishit Parekh, Michael Dickey, and Lilian C. Hsiao*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States*

Gallium and its alloys form a native oxide layer, which acts like a skin that encapsulates the liquid metal. There has been a surge in interest on investigation of gallium and its alloys as electronic materials for their potential applications, in flexible and stretchable electronics, due to low toxicity, high metallic conductivity, and its compatibility with soft materials such as organic polymers during processing. Despite the immense potential of liquid metals, there is a lack of understanding of the viscoelastic nature of the oxide skin. In this work, we characterize the oxide skin at liquid metal-air interfaces using a Du Nöuy ring attached to a stress-controlled rheometer. A systematic study of the interfacial oxide layer is performed by following the linear elastic and viscous moduli for pristine gallium, its alloys with indium and tin, eutectic gallium indium and galinstan. Additionally, the pristine liquid metals when doped with aluminum at a weight percent as low as 0.45%, modifies the liquid metal-air interface. Our results show a time evolution of the liquid metal-air interface when aluminum diffuses from the bulk liquid metal matrix and migrates to the liquid metal-air interface replacing gallium to form an oxide layer with elastic moduli that is larger than the undoped liquid metal alloys. Finally, using imaging and analytical characterization tools such as scanning electron microscopy, energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy, qualitative and quantitative insights are gained into the skin texture and composition of elements in pristine as well as doped oxide layers of gallium that leads to the change in viscoelasticity of the skin. This work could provide a pathway to modifying the rheology of liquid metal for printing as well as tuning the chemistry of the interface of the metal for use as soft electrodes.

Wednesday 3:45 Tanglewood

FE14

**Single droplet interfacial measurements using microfluidic extensional flows**Shweta Narayan<sup>1</sup>, Davis B. Moravec<sup>2</sup>, Brad G. Hauser<sup>2</sup>, Andrew J. Dallas<sup>2</sup>, and Cari S. Dutcher<sup>1</sup><sup>1</sup>*Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, United States;* <sup>2</sup>*Donaldson Company, Bloomington, MN 55431, United States*

Micron-sized droplets, dispersed in complex oil-water emulsions, can be challenging to separate using conventional coalescing techniques. The presence of surfactants which lower interfacial tension between the dispersed and continuous phases further increases the difficulty to coalesce and separate these droplets. In previous work, we show using a dynamic microfluidic tensiometer, that the timescale for equilibration of dynamic interfacial tension scales strongly with droplet size. In addition to lowering interfacial tension, surface-active components confer viscoelastic properties to the oil-water interface. The most popular methods for measuring interfacial rheological properties include the double-wall ring geometry for interfacial shear rheology, and oscillating bubble technique or the more recently developed microtensiometer by Alvarez et al. for dilatational rheology. Here, we employ a microfluidic platform with an extensional flow field coupled with shape oscillation analysis for performing interfacial measurements on complex oil-water interfaces. This technique will be applied towards measuring interfacial rheological properties of complex liquid-liquid interfaces. These measurements will provide fundamental insights into the rheological behavior of complex interfaces in emulsions, at length and time scales relevant to liquid-liquid separation applications

Wednesday 4:10 Tanglewood

FE15

**Tears of wine**Prerana Rathore, Chenxian Xu, and Vivek Sharma*Chemical Engineering, University of Illinois in Chicago, Chicago, IL, United States*

'Tears of wine' refer to the rows of wine-drops that spontaneously emerge within a glass of strong wine. Evaporation-driven Marangoni flows near the meniscus of water-alcohol mixtures drive liquid upward forming a thin liquid film, and a rim forms near the moving contact line. Eventually the rim undergoes an instability, thus forming drops, that roll back into the bulk reservoir as the so-called tears of wine. Most studies in literature argue the evaporation of more volatile, lower surface tension component (alcohol) results in a concentration-dependent surface tension gradient that drives the climbing flow within the thin film. Though it is well-known that evaporative cooling can create temperature gradients that could provide additional contribution to the climbing flows, the role of thermocapillary flows is less well-understood. Furthermore, the patterns, flows and instabilities that occur near the rim, and determine the size and periodicity of tears, are not well-studied. Using experiments and theory, we

visualize and analyze the formation and growth of tears of wine. The sliding drops, released from the rim towards the bulk reservoir, show oscillations and a cascade of fascinating flows that are analyzed for the first time.

Wednesday 4:35 Tanglewood

FE16

### **Understanding interfacial structure and flow properties of protein-surfactant systems at the air-water interface**

Ying-Heng S. Tein<sup>1</sup>, Michael Zhang<sup>1</sup>, Yun Liu<sup>2</sup>, Ann M. Woys<sup>3</sup>, Isidro Zarraga<sup>3</sup>, and Norman J. Wagner<sup>1</sup>

<sup>1</sup>*University of Delaware, Newark, DE, United States;* <sup>2</sup>*Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, United States;* <sup>3</sup>*Department of Late Stage Pharmaceutical Development, Genentech Inc, San Francisco, CA, United States*

Monoclonal antibodies (mAbs) are important therapeutic agents, but vial shipments of their formulations have posed challenges associated with stability issues due to adsorption of mAbs at the air-water interface, which is thought to be aggregation driven. Formulators add surfactants that are active at the air-water interface, such as polysorbate 20 (PS20) to prevent protein adsorption and to increase protein stability. Because both mAb and surfactant affect the interfacial mechanical properties, it is important to characterize the interface for vial filling, shipment, and drug delivery processes. Furthermore, both apparent shear thinning and elasticity behavior detected in rotational rheometry of pure mAb solutions have been speculated to derive from mAb interfacial activity. For example, Patapoff and Esue used cone-and-plate rheometry to observe a decrease in elasticity with the addition of PS20 in mAb solutions and hypothesized that surface active agents “protect” the interface to prevent interfacial activity of mAb. However, only limited interfacial measurements have directly characterized the nanoscale structure of the interface for mAb/PS20 solutions [2]. To test the hypothesis that PS20 stabilizes mAbs by protecting the air-water interface, we directly characterize these solutions through neutron reflectivity, interfacial rheology and surface tensiometry. These results reveal the interfacial viscoelasticity and orientation of the mAb at the air-water interface as well as demonstrate how PS20 effectively prevents mAb adsorption. Additionally, we reflect on future investigations of measuring interfacial dilatational rheology to mimic bubble formations in solution in order to minimize protein instabilities at air-water interfaces.

[1] Patapoff, T. W., & Esue, O. (2009). *Pharm Dev Technol.*, 14(6), 659-664. [2] Leiske, D.L., Shieh, I.C., Tse, M.L., (2016), *Langmuir* 32:9930-9937.

Wednesday 5:00 Tanglewood

FE17

### **Foam films and liquid bridges formed by aqueous sodium naphthenate solutions**

Chrystian Ochoa, Yiran Zhang, Jelena Dinic, William Yang, Subinuer Yilixiati, and Vivek Sharma

*Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

Sodium Naphthenates found in crude oils can act as surfactants, and self-assemble in aqueous solutions to form micelles and liquid crystals. Understanding and controlling the drainage kinetics of thin films is an important problem that underlies the stability, lifetime and rheology of petroleum foams and emulsions. Here we show that foam films formed by aqueous solutions of sodium naphthenates exhibit step-wise thinning or stratification, due to the influence of non-DLVO forces, including supramolecular oscillatory structural forces. We utilize Interferometry, Digital, Imaging, Optical Microscopy protocols, previously developed by our group, to investigate the drainage and stratification in micellar foam films (< 100 nm) with high spatial (thickness < 10 nm) and temporal resolution (< 1 ms). We determine how the concentration of added sodium naphthenates influences the nanoscopic topography, stratification kinetics and step size of foam films and contrast the results with behavior observed with stratifying foams made with sodium dodecyl sulfate (SDS) solutions. Finally, we show that visualization and analysis of capillary-driven thinning and pinch-off dynamics of the columnar neck in an asymmetric liquid bridge created by dripping-onto-substrate (DoS) of sodium naphthenate solutions can be used for characterizing the change in shear viscosity, extensional viscosity and microstructure in such surfactant solutions.

## **Symposium NF Non-Newtonian Fluid Mechanics & Flow Instabilities**

Organizers: Aditya Khair and Christian Clasen

Wednesday 1:30 Plaza II

NF19

### **Acoustically enhanced bubble removal from yield-stress fluids**

Marco De Corato, Brice Saint-Michel, and Valeria Garbin

*Department of Chemical Engineering, Imperial College London, London SW72AZ, United Kingdom*

Yield-stress fluids are encountered in many industrial areas such as formulated products, oil recovery, and wastewater treatment. In these applications, small gas bubbles are often generated or trapped while processing the fluid. Once suspended in a yield-stress fluid, micron-sized bubbles are difficult to remove because their buoyancy force is below the yield stress. The presence of trapped bubbles may affect the product quality or process performance, hence methods for removal of bubbles from yield-stress fluids are desirable. We explore the use of ultrasound to release micron-sized bubbles from yield-stress fluids. Preliminary experiments performed in our lab suggest that micron-sized bubble can become free to escape after less than a minute of exposure to ultrasound. We hypothesize that the radial oscillations of the bubbles in the ultrasound field cause local yielding. We develop a theoretical framework to describe the deformation of yield-stress fluids by oscillating microbubbles. We modify the Rayleigh-Plesset equation governing the radial dynamics of the bubble to take into account the complex behaviour of the fluid. We characterize

the amplitude of the radial oscillations of the bubble as a function of the ultrasound frequency, and for different rheological parameters, by solving the Rayleigh-Plesset equation numerically. By quantifying the volume of fluid that is yielded as a function of the amplitude and frequency of the acoustic pressure, it is possible to predict optimal conditions for bubble removal.

Wednesday 1:55 Plaza II

NF20

### **Buoyancy effects on micro-annulus formation: Fluid-fluid displacements in vertical channels**

Ian A. Frigaard and Marjan Zare

*University of British Columbia, Vancouver, British Columbia V6T1Z4, Canada*

Buoyant miscible displacement flow of a Bingham fluid by a Newtonian fluid along a vertical plane-channel is studied, in the high Peclet number regime for both density stable and density unstable regimes. The flow is effectively governed by 4 dimensionless parameters: the Newtonian Bingham number ( $B_N$ ), the viscosity ratio ( $m$ ), the Reynolds number ( $Re$ ), and modified Froude number ( $Fr$ ). This is a simple model for micro-annulus formation in the primary cementing of oil and gas wells. The micro-annulus layers correspond to residual drilling mud that remains on the walls after displacement. We give the main characteristics of density stable displacements, which result in stable symmetric flows for the parameters studied. We then show that in density unstable situations static residual wall layers can exist for yield stresses below the minimum for density stable regimes. These layers are partially static and may also be thicker than the fully static layers encountered in density stable flows. Large  $B_N$  stabilizes the flow. Adverse buoyancy gradients ( $Re/Fr^2$ ) seem to promote instability of the flow. These instabilities are various, ranging from Rayleigh-Taylor type frontal instabilities, through to Kelvin-Helmholtz type inertial waves ( $m \leq 1$ ) and more viscous-controlled inverse bamboo and mushroom morphologies ( $m > 1$ ). We present an overview of flow regimes within our parameter space and give approximate onset criteria. It remains unclear whether or not the instabilities observed result in improved fluid displacement efficiency.

Wednesday 2:20 Plaza II

NF21

### **Law of resistance for viscoelastic fluids in channel flows at low $Re$**

Paulo E. Arratia and Boyang Qin

*Mechanical Engineering & Applied Mechanics, University of Pennsylvania, Philadelphia, PA, United States*

In this talk, we investigate the flow of a polymeric fluid in a straight micro-channel at low  $Re$  using pressure drop measurement and particle tracking methods. Pressure measurements show that the flow resistance increases as the flow transitions from stable/laminar to a “turbulent-like” state. This behavior is analogous to Newtonian fluids where the friction factor increases as the flow transitions from laminar to turbulent except that here the governing parameter is the Weissenberg number ( $Wi$ ). The increased in flow resistance suggests the presence of flow structures. We find that tracer particles in the parallel shear region follows wavy trajectories with strong spanwise modulation not found in the stable unperturbed flow. Statistics of the secondary velocity component clearly suggest the presence of flow structures taking place far downstream in the parallel shear region. We believe that the increase in flow resistance is connected to the appearances of these wavy particle motions. As a result, the flow resistance, as measured by pressure head required to sustain the flow, increases markedly relative to the laminar flow.

Wednesday 2:45 Plaza II

NF22

### **Roles of elasticity and inertia in the flow of polymer solutions around a sharp bend**

Michael Cromer<sup>1</sup> and Larry Villasmil<sup>2</sup>

<sup>1</sup>*School of Mathematical Sciences, Rochester Institute of Technology, Rochester, NY 14618, United States;* <sup>2</sup>*Dept. of Manufacturing and Mechanical Eng. Tech., Rochester Institute of Technology, Rochester, NY, United States*

Generally, vortex formation occurs due to geometrical singularities located at both salient and re-entrant corners. In the former, viscoelastic stresses are infinitesimal, on the other hand, stresses occurring in the latter region are extremely high under which some viscoelastic fluids exhibit fundamentally different constitutive flow behavior. Flow separation from solid boundaries caused by the inability of the material to sustain stress can occur in some polymer melts. For low flow rates, polymer flow is steady with small viscous vortex and no elastic vortex. As the flow rate increases, an elastic vortex begins to form (independent of the viscous vortex). This elastic “lip vortex” has also been observed in abrupt contraction and cross-slot flows. In order to isolate the role of shear flow, Susan Muller's group at Berkeley considered the flow around a 90-degree bend. They were able to experimentally show that shear thinning is necessary for the formation of the lip vortex. In this work, we simulate non-Newtonian fluid flow around a sharp bend, using several polymeric constitutive models (e.g., Oldroyd-B, FENE-P, Giesekus), in order to predict the roles played by elasticity (namely shear thinning) and inertia. In the absence of inertia, we are able to confirm the hypothesis that shear thinning is necessary for the formation of an elastic lip vortex. However, we further show that it is not a sufficient condition: as the degree of shear thinning increases, the size of the vortex decreases (until disappearing). As an extension of this work, we also considered one particular example of the elastic lip vortex and simulated the behavior of the flow when the polymer concentration (inertia) is decreased (increased). Ultimately, we find a transition from the upstream (elastic) vortex to a downstream (inertial) vortex, expected for Newtonian fluids. Phase diagrams reveal operating windows within which one can find the elastic vortex, the inertial vortex or no lip vortex at all.

Wednesday 3:45 Plaza II

NF23

**Viscous fingering instabilities in carbon black gels**Badis Marsit<sup>1</sup>, Yacouba Kaloga<sup>1</sup>, Irmgard Bischofberger<sup>1</sup>, and Thibaut Divoux<sup>2</sup><sup>1</sup>*Mechanical Engineering, MIT, Cambridge, MA 02139-4307, United States;* <sup>2</sup>*MSE2, CNRS Bordeaux, CNRS-MIT, Cambridge, MA, United States*

Pattern formation in fluids occurs in numerous physical processes in which mechanical mixing, chemical reactions, evaporation and/or surface effects play a key role. When the pattern develops in a non-Newtonian fluid, the non-linear rheology interferes with the patterning process, which often generates a richer dynamics than that commonly observed for a Newtonian fluid. Here we focus on the viscous fingering instability in a time-dependent yield stress fluid. We study experimentally the flow of a carbon black gel sandwiched in a parallel plate geometry, for which the upper plate is being lifted up at constant velocity. We show the existence of a critical initial gap spacing and a critical lift velocity, above which the flow becomes unstable, leading to the growth of viscous finger originating from the Saffman-Taylor instability at the fluid-air interface. The resulting pattern in the gel consists in a tree-like branched structure, and covers only a fraction of the plate surface. Varying the gel concentration, we demonstrate that the extent of the pattern is governed by the yield strain of the carbon black gel, while for a fixed gel concentration, the span of the pattern increases for increasing lift velocity and decreasing initial gap width. Moreover, we observe three different regimes in the selection of the wavelength: a yield stress dominated regime, a viscous dominated regime and a surface tension dominated regime. Finally, we show that the shear history of the gel has a strong influence on the pattern morphology and allows us to generate a broad variety of patterns, from heavily ramified structures composed of thin branches when the gel is rejuvenated by a preshear of high intensity followed by an abrupt flow cessation, to coarse patterns characterized by a large core and a few thicker branches when the gel is rejuvenated by a preshear of high intensity followed by a slow cessation of shear.

Wednesday 4:10 Plaza II

NF24

**Effect of viscoelasticity on the hole growth dynamics in a liquid curtain**Marisa S. Bazzi<sup>1</sup>, Alireza M. Karim<sup>2</sup>, Wieslaw Suszynski<sup>2</sup>, Francis Lorraine<sup>2</sup>, and Marcio S. Carvalho<sup>1</sup><sup>1</sup>*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451900, Brazil;* <sup>2</sup>*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States*

Thin liquid sheets appears in wide range of practical applications such as atomization, paper manufacturing, and curtain coating. In curtain coating, a thin liquid sheet is formed and falls under the influence of gravity over a considerable height before it impinges onto a moving substrate. Liquid curtain breaks below a critical flow rate, which is a function of the liquid properties. The breakup is a result of a very fast sequence of events: a small perturbation on the liquid interface grows and pinches-off the curtain, creating a small hole. Capillary forces expand the hole causing the curtain disintegration. The effect of viscoelastic forces on the hole growth speed in a liquid curtain was studied by high-speed visualization and a mathematical model based on mass and momentum conservation equations coupled with the Oldroyd-B constitutive model, modified by the long-wave theory. Different Boger-like aqueous solutions were used as the viscoelastic liquids in the visualization experiments. The results show the stabilizing effect of viscoelastic stresses on the capillary-driven hole growth and how liquid rheology may be optimized in order to achieve thinner coated films using curtain coating process.

Wednesday 4:35 Plaza II

NF25

**Microrheology and kinematics of a drying paint**Selwin M. Varghese<sup>1</sup>, Reza M. Rock<sup>2</sup>, James F. Gilchrist<sup>3</sup>, and Christopher L. Wirth<sup>1</sup><sup>1</sup>*Chemical and Biomedical Engineering, Cleveland State University, Cleveland, OH, United States;* <sup>2</sup>*PPG Industries, Allison Park, PA, United States;* <sup>3</sup>*Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA, United States*

Controlling the rheological behavior of a coating is crucial to improving coating aesthetics and performance. However, the transient rheological properties of a coating during the flash and cure process are often difficult to measure and, consequently, not well understood. Microrheology, a technique that uses nano- to micrometer scale probe particles for a rheological measurement, is one potential non-invasive technique for probing the transient material properties of a drying paint. Passive microrheology was used to probe films at both steady (non-drying) and unsteady (drying) conditions. Particles were successfully tracked and imaged in both clear and cloudy coatings, using fluorescent microparticle probes. Drying behavior was observed by tracking the decrease in logarithmic slope of the mean squared displacement (MSD) at time points during drying for films of thickness 100 and 150  $\mu\text{m}$ . Thinner films were observed to more quickly decrease in logarithmic MSD slope, or increase in viscosity. These results demonstrate the feasibility of an in-situ technique for probing a drying coating and also how parameters such as coating thickness affected the rheological properties of the coating.

Wednesday 5:00 Plaza II

NF26

**Discontinuous shear thickening of polar liquid crystals**Tomer Markovich<sup>1</sup>, Elsen Tjhung<sup>2</sup>, and Michael E. Cates<sup>2</sup><sup>1</sup>*Center for Theoretical Biological Physics, Rice University, Houston, TX, United States;* <sup>2</sup>*DAMTP, University of Cambridge, Cambridge, United Kingdom*

Molecular polar liquid crystals are rather rare in nature, hence, they were not thoroughly investigated as other liquid crystalline phases. However, recently, the growing field of active matter required their investigation as polar liquid crystals are common in active biological systems. In this work we study passive polar liquid crystals under shear. We find that the shear alignment parameter affects the polar order parameter in the same

manner it affects the nematic director, i.e., it defines the Leslie angle. However, the polar order parameter is not of fixed size, and thus a new shear elongation parameter is introduced. The latter may even cause shear to act counterintuitive and reduce the polar order in some cases. The steady state solution of the equations of motion (for the polar order parameter and the Navier-Stokes equation) further reveals that the sheared system can be described by an effective free-energy. Using this effective free energy, we obtain analytically an intriguing phase diagram that reveals how the ratio of the shear alignment and shear elongation parameters defines the order of isotropic-polar transition. Finally, we use the rate of heat dissipation to calculate the effective viscosity and find it to depend on the modulus of the polar order parameter. Because the latter is a complex function of the shear rate, polar liquid crystals may show shear thinning or shear thickening, and a possibility of discontinuous shear thickening arise. These analytical findings agrees perfectly with our direct numerical simulations.

## Thursday Morning

### Symposium AP Award Presentations

#### *Metzner Award Presentation*

Thursday 8:00 Galleria I

AP1

#### **Memory effects in colloidal gels**

Thibaut Divoux

*MSE2, CNRS Bordeaux, CNRS-MIT, Cambridge, MA, United States*

Gelation of colloidal suspensions plays a crucial role in the formation of numerous materials. Examples range from cement to yogurt, which result respectively from the aggregation of CSH nanoparticles and casein micelles. In both systems, short-range attractive interactions between particles lead to the formation of a percolated network that is responsible for the solid-like behavior of the material at rest. Generated by a kinetic arrest, these solids are metastable out-of-equilibrium structures, whose properties are sensitive to the route followed during gelation. In that context, external shear often comes to compete with the attractive interactions that drives the gelation, affecting the gel microstructure, which encodes the shear history. In this talk, I will discuss various aspects of shear-induced memory effect in colloidal gels. First, I will illustrate a way to quantify the gel's memory through the so called rheological hysteresis. Indeed, the constitutive equation of colloidal gels, i.e. shear stress versus shear rate, is generally obtained by sweeping up or down the shear rate over a finite temporal window. In general, the up and down sweeps do not superimpose and define a rheological hysteresis loop, which can be used to define a single timescale characteristic of the gel. Second, limiting the previous protocol to a single down sweep that brings the gel from a fluidized state to a complete stop, I will show that flow cessation can be used to tune the structural and mechanical properties of gels. Indeed, rheo-electric measurements reveal that abrupt flow cessation leads to strong and connected gels, whereas slow ramps lead to softer and less-conductive gels, a signature of lower connectivity in the sample-spanning network. This scenario is robust and data obtained with various flow cessation protocols and different particle concentrations collapse on a master curve that could be useful for the design of colloidal-based materials.

### Symposium SC Suspensions & Colloids

Organizers: Giovanniantonio Natale and Roseanna N. Zia

Thursday 8:40 Galleria I

SC40

#### **Diving into a shear-thickening bath**

Philippe Bourrienne and Gareth H. McKinley

*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Shear-thickening fluids, formulated from high volume fraction suspensions of micro or nanoparticles, react to imposed excitations with a tunable behavior. At low shear rates, they flow like a Newtonian or weakly shear-thinning liquid, whereas they rapidly stiffen following a more rapid perturbation. When a solid object impacts a bath of shear-thickening fluid, the initial velocity determines the different settling regimes that are observed. We will describe these different regimes with regard to the rheological properties of the shear-thickening liquid and the characteristics of the impacting object. A few surprising observations could be noticed. First, a high velocity is not always the best way to penetrate such suspensions. Under such conditions, an appropriately-shaped fast-moving object can also bounce during the impact due to the shear-thickening behavior. For those objects that do penetrate the liquid, the sedimentation process may also be discontinuous or exhibit aperiodic oscillations due to dynamical interactions between the timescale characterizing the rate of shear-thickening and the inertia of the sedimenting particle.

Thursday 9:05 Galleria I

SC41

#### **Linear viscoelasticity of colloidal suspensions from probe rheology simulations: Application to nanoscopic systems**

Dinesh Sundaravivelu Devarajan and Rajesh Khare

*Department of Chemical Engineering, Texas Tech University, Lubbock, TX, United States*

The wide-spread industrial applications of colloidal suspensions have led to a significant interest in understanding their structure, flow, and end-use properties. Rheology of nanocolloidal dispersions is governed by interparticle interactions; molecular simulations provide a tool for investigating these effects. Previously, for polymer melts, we showed that the simulated nanoparticle motion in those systems can be analyzed using the inertial generalized Stokes-Einstein relation (IGSER) to predict the linear viscoelasticity of the medium. In this work, we have applied the same formalism to colloidal systems in both the active and the passive modes. The colloidal volume fraction ( $\phi$ ) range investigated in this

study covers the regime from dilute suspensions to concentrated suspensions up to the liquid/solid transition point. Dynamic modulus values obtained by analyzing the nanoparticle motion using IGSER are shown to be in good agreement with those calculated from the non-equilibrium molecular dynamics (NEMD) simulations of the same system. Calculated dynamic viscosity values are also found to be consistent with the literature experimental values. In the oscillatory active nanorheology molecular simulations, colloidal distribution around the probe was studied in the context of the Peclet number (Pe) and the oscillation rate ( $\alpha$ ). Results will also be presented for different size ratios of probe and colloidal particles.

Thursday 9:30 Galleria I

SC42

### **Shear-induced migration and segregation of concentrated bidisperse suspensions in Poiseuille flows**

Byoungjin Chun, Jin Seok Park, and Hyun Wook Jung

*Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea*

Although particle segregation in flowing polydisperse suspensions is encountered in many natural and industrial processes, it has been not well understood how the concentration profiles of suspended particles evolve under the inhomogeneous shear flow fields. In this study we investigate particle dynamics in concentrated bidisperse suspensions under Poiseuille flows between two plates, employing the lattice Boltzmann method, emphasizing on shear-induced migration and segregation features. In the plane Poiseuille flows, neutrally buoyant and non-Brownian bidisperse particles of volume fraction 0.3 are mainly considered. A series of simulations were performed to characterize particle migration and segregation, including effects of concentration and size ratio of bidisperse particles. The phenomena were also interpreted by a continuum model, the diffusive flux model. The time-dependent concentration profiles obtained by both model and simulation showed quite good agreement each other with optimized values of coefficients in the model. One of interesting findings is that the segregation time scale for the suspensions is several times longer than their migration time scale.

Thursday 10:25 Galleria I

SC43

### **Conformation tensor-based macroscopic models of particulate and multiphase systems**

Paul M. Mwasame<sup>1</sup>, Norman J. Wagner<sup>2</sup>, and Antony N. Beris<sup>2</sup>

<sup>1</sup>*Sullivan Park Science & Technology Center, Corning Incorporated, Erwin, NY 14870, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Recently [1], the Maffettone-Minale model for dilute emulsions has been recast and extended for arbitrary (dispersed/continuum) viscosity ratios using the non-equilibrium thermodynamics bracket framework [2]. More recently, we also developed a generalization of that model for conditions where particle inertia effects are important [3]. In both cases, all the model parameters have been obtained based on comparisons against previous asymptotic microscopic theory results. In the present work, we offer two additional extensions. In the first one, we describe how a two conformation tensors-based model can be developed through which we can describe the rheology of emulsions in the presence of Ostwald ripening. We are thus able to describe a population of droplets and their evolution in time along with the evolution of the rheology. In the second application, a model for the rheology of concentrated non-Brownian suspensions is presented. Following Phan-Thien [4], the microstructure is represented through a conformation tensor that represents now the second moment of the unit vector along the center to center line connecting two generic spheres. However, unlike that work, the thermodynamically-based model formulated here following an extension of the bracket approach of [2] is consistent with all viscometric functions in non-Brownian suspensions. In shear flows, the model predicts negative first and second normal stress differences that have been observed in both experimental and simulation studies. These are accompanied by microstructure orientation and localization along the compressional axis of the shear flow field.

Acknowledgment: NSF, Grant No. CBET 312146.

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Thursday 10:50 Galleria I

SC44

### **The dynamics of confined paramagnetic colloidal chain**

Kedar Joshi and Sibani Lisa Biswal

*Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

We experimentally studied the microstructure of a semiflexible colloidal chain confined in an emulsion droplet. Isotropic confinement is offered by creating colloidal chains inside an emulsion droplet, followed by its controlled shrinking. The chain length and flexibility can be varied by varying the particle concentration and linker (DNA) length. As the droplet shrinks, various microstructure states can be observed. The chain follows a certain configurational path depending on the size of chain (number of particles), its persistence length, and the droplet's shrinking rate. We characterize these microstates by measuring the chain diffusivity and bending energy as a function of droplet size and shrinking rate. Interestingly, configurations that had a higher initial bending energy resulted in confined configurations that were of lower energy. This work will help in visualizing folding and collapse of semi-flexible filaments in a particular environment.



Thursday 11:15 Galleria I

SC45

**A viscoelastic modification to the Modified Delaware Thixotropic Model (MDTM)**Matthew J. Armstrong<sup>1</sup>, Norman J. Wagner<sup>2</sup>, and Antony N. Beris<sup>2</sup><sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Recent work using small angle neutron scattering under flow has identified the existence of a microstructure that is dependent on flow conditions [1,2] in soft colloidal systems. On the other hand, over the last twenty years or so, a large number of empirically based thixotropic, rheological models has been developed that involve, albeit phenomenologically, a single scalar structural parameter,  $\lambda$  [3-6]. These models involve the combination of a  $\lambda$ -dependent decomposition of the shear stress to an elastic and a viscous contribution with a relaxation-based evolution equation for  $\lambda$ . The rich behavior of the soft colloidal systems is primarily due to the interaction of the structure and the hydrodynamic force and this can be particularly enhanced applied through in transient flow, and/or large amplitude oscillatory shear flow. Applying large amplitude oscillatory shear (LAOS), and other transient flow conditions to complex fluids induces rheological responses, that, with proper modeling, can be used to sensitively probe the underlying microstructure and its dynamics. We demonstrate this for several colloidal systems including thermoreversible gel, fumed silica, carbon black and human blood while using a newly developed semi-empirical, thixotropic master-equation, with a novel viscoelastic modification developed around a scalar internal structural parameter using the recently published Modified Delaware Thixotropic Model as a basis [3,4,5,6].

[1] C.R. Lopez-Barron, A.K. Gurnon, A.P.R. Eberle, L. Porcar, and N.J. Wagner. *Physical Review* 89, 042301 (2014), 1-11. [2] J. M. Kim. PhD thesis, University of Delaware, 2013. [3] J. Mewis and N. J. Wagner, *Colloidal Suspension Rheology*, Cambridge Univ. Press (2012). [4] P. de Souza Mendes and R. Thompson. *Rheol. Acta* (2013) 52:673-694. [5] A. Mujumdar, A. N. Beris and A. B. Metzner. *J. Non-Newtonian Fluid Mech.* 102 (2002). [6] C.J. Dimitriou, R.H. Ewoldt and G.H. McKinley. *J. Rheol.* 571(1), (2013).

**Symposium PM****Polymer Melts: From Molecular Rheology to Processing**

Organizers: Reza Foudazi and Richard Graham

Thursday 8:40 Plaza I

PM27

**Gap spanning spherulitic clusters during isothermal crystallization of polypropylene**Debjani Roy, Debbie Audus, and Kalman Migler*Polymer, NIST, Gaithersburg, MD 20899, United States*

We use a rheometer equipped with an optical module to correlate the evolution of modulus and morphology during quiescent isothermal crystallization of an isotactic polypropylene (iPP). The morphology, the nucleation density, and the growth rate of both bulk and surface nucleated spherulites were monitored during experiments performed under quiescent conditions. We found that varying the gap thickness strongly changes the timescale for the sharp upturn in transient modulus. To understand this gap dependence we perform 3D reconstructions of the spherulitic morphologies with an emphasis on assessing the relative importance of surface vs. bulk effects. As the spherulites nucleate and grow, they impinge and form clusters which eventually span the width of the gap. We analyze this via generalized effective medium (GEM) theory which allows computation of a critical percolation threshold. Furthermore, we find that the elastic modulus is sensitive to such clusters and describe the dimensionless parameters that govern this behavior.

Thursday 9:05 Plaza I

PM28

**Flow induced crystallisation in polymers: From molecules to processing**Richard S. Graham*School of Mathematical Sciences, University of Nottingham, Nottingham, United Kingdom*

Flow profoundly influences the crystallisation kinetics and morphology of polymeric materials. By distorting the configuration of polymer chains, flow breaks down the kinetic barriers to crystallisation and directs the resulting crystallisation. This flow-induced crystallisation (FIC) in polymers is a fascinating, externally driven, non-equilibrium phase transition, which is controlled by kinetics. Furthermore, the effect is of central importance to the polymer industry as crystallisation determines virtually all of the useful properties of semi-crystalline polymer products. However, simulating and modelling flow-induced crystallisation in polymers is notoriously difficult, due to the very wide spread of length and timescales. I will present results from an ongoing multi-scale modelling project. Our project combines molecular dynamics simulations of nucleation, highly coarse-grained simulations of nucleation, continuum-level nucleation models, a polydisperse tube model for non-linear flow and finite element modelling of polymer processing. I will summarise current results and connections between the modelling techniques. I will also present some experimental data from the same project.

Thursday 9:30 Plaza I

PM29

### **Formation and reactivation of flow-induced crystallization precursors in semi-crystalline engineering thermoplastics**

Alicyn M. Rhoades<sup>1</sup>, Jiho Seo<sup>2</sup>, Anne M. Gohn<sup>1</sup>, René Androsch<sup>3</sup>, and Ralph H. Colby<sup>2</sup>

<sup>1</sup>Plastics Engineering Technology, Penn State Behrend, Erie, PA 16563, United States; <sup>2</sup>Materials Science and Engineering, The Pennsylvania State University, University Park, PA, United States; <sup>3</sup>Interdisciplinary Center for Transfer-oriented Research in N, Martin Luther University Halle-Wittenberg, Halle Salle, Germany

Typical manufacturing techniques first subject a semi-crystalline polymer melt to flow, while the majority of polymer crystallization occurs upon cessation of flow. Brief intervals of shear flow at rates exceeding the reciprocal of the Rouse time of the longest chains create precursors that nucleate orders of magnitude more crystals and change the resulting morphology from ~30  $\mu\text{m}$  spherulites to far smaller ~1  $\mu\text{m}$  crystallites or to long shish-kebab structures, depending on the previous shear work input. In this study, the flow-induced crystallization (FIC) of polyamide 66 (PA 66) and poly (ether ether ketone) (PEEK) have been studied using parallel plate and capillary rheology. In order for PA 66 to experience FIC the polymer must be subject to at least 40 kPa of shear work, which is also coincident with the failure of the Cox-Merz rule. After rheological study, the polymer samples were removed and then investigated using fast scanning calorimetry (FSC) and polarized light microscopy. For PA 66, the crystalline precursors formed in the rheometer are sufficiently stable to nucleate subsequent crystallization in the FSC, and it was determined that the rate of crystallization increases as a function of previous shear work input at low and medium levels of supercooling where heterogeneous nucleation dominates. At high supercooling where homogeneous nucleation dominates, previous shear work did not influence the speed of crystallization. Differences between PA 66 and the more rigid PEEK polymer will be discussed.

Thursday 10:25 Plaza I

PM30

### **SAXS/WAXS studies of flow-induced crystallization of poly(lactic acid) under uniaxial extensional flow**

Mu Sung Kweon<sup>1</sup>, Wesley Burghardt<sup>1</sup>, Amirjalal Jalali<sup>2</sup>, and Michel Huneault<sup>3</sup>

<sup>1</sup>Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, United States; <sup>2</sup>Mechanical & Industrial Engineering, University of Toronto, Toronto, Ontario M5S 3G8, Canada; <sup>3</sup>Chemical Engineering and Biotechnology Engineering, University of Sherbrooke, Sherbrooke, Quebec J1K 2R1, Canada

We report flow-induced crystallization studies of branched PLA under uniaxial extensional flow. Flow was applied using an SER housed in a custom-built oven designed to facilitate *in situ* synchrotron x-ray experiments. Samples loaded onto the fixture were first heated well into the melt, then cooled to a selected crystallization temperature at which quiescent crystallization was suppressed at early times. A short burst of uniaxial extensional flow was applied and the subsequent crystallization behavior was monitored using simultaneous SAXS and WAXS measurements. Overall, SAXS and WAXS data gave remarkably consistent results for both the extent of crystallization and the degree of crystallite orientation. Increasing the extension rate at a constant applied Hencky strain generally led to faster crystallization kinetics as well as higher degrees of crystallite orientation. Similar qualitative behavior was observed with increasing the applied strain at a fixed extension rate.

Thursday 10:50 Plaza I

PM31

### **Viscoelasticity-crystallinity relationships for flow-induced crystallization in polycaprolactone**

Anthony Kotula

Materials Science and Engineering, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

The effect of shear flow on polymer crystallization processes are well-known but poorly understood. Of critical importance to industrial polymer processes is the relationship between rheology and crystallinity when crystallization occurs either during or after a period of shear. Measurements of crystallinity and rheology are commonly performed on separate instrumentation, but variation in temperature control and sample preparation for different instruments make correlation challenging. To address this issue, we perform simultaneous measurements of optical microscopy, Raman spectroscopy, and shear rheology during crystallization from the melt state after a period of shear (~1 s<sup>-1</sup>) at elevated temperatures near the equilibrium melting temperature. The crystallinity is quantified via Raman spectroscopy while structure growth is monitored by the appearance of birefringent material. Simultaneous measurements of crystallinity and rheology allow us to generate modulus-crystallinity plots that demonstrate the effects of angular frequency and shear on the sensitivity of the modulus to increasing crystallinity. We show where the experimental results are well-fit by the general effective medium equation - a suspension-based model that incorporates a percolation threshold of volume-spanning semicrystalline domains. Our results indicate that the critical percolation fraction and scaling near the percolation transition depend on shear applied in the melt state.

Thursday 11:15 Plaza I

PM32

**Anisotropic thermal transport in non-linear-non-isothermal polymeric flows**David Nieto Simavilla<sup>1</sup>, David Venerus<sup>2</sup>, Jay D. Schieber<sup>3</sup>, Doros N. Theodorou<sup>4</sup>, and Wilco M. H. Verbeeten<sup>1</sup><sup>1</sup>*SIRG Department of Civil Engineering, Universidad de Burgos, Burgos, Castilla y León 09006, Spain;* <sup>2</sup>*Chemical and Biological Engineering, Illinois Institute of Science and Technology, Chicago, IL, United States;* <sup>3</sup>*Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States;* <sup>4</sup>*Chemical Engineering, National Technical University of Athens, Athens, Attika, Greece*

Over the last decades, significant efforts have been dedicated to include more complete rheological constitutive models into finite elements methods to simulate the complex flows in polymer manufacturing. However, while a remarkable portion of these processes are intrinsically non-isothermal, the study and implementation of non-isothermal flows has been very limited. The degree of complexity of such calculations is considerably increased by: 1) the addition to the problem of the energy equation; 2) a strong coupling to the momentum balance due to a highly temperature-dependent rheological behavior and 3) the strong influence that deformation-induced molecular orientation has on the thermo-physical properties of polymeric materials. Experimental evidence has shown that thermal conductivity becomes anisotropic in polymers subjected to deformation. Furthermore, a linear relationship between the thermal conductivity and stress tensors has been found to be universal (i.e. independent of polymer chemistry) and to extend beyond the finite extensibility limit. We make use of molecular simulation techniques to gain insights into the transport mechanisms behind these surprising results. On a more practical level, our work combines the thermal conductivity/stress response with two recent constitutive equations proposed for linear (Rolie Poly) and branched (eXtended Pom-Pom) polymers to venture predictions for the anisotropy in thermal conductivity in a number of interesting flows. These two constitutive models provide accurate descriptions of the available non-linear rheology and thermal transport data. Remarkably, our approach allows implementation of anisotropy in thermal conductivity into finite elements simulations without adding any adjusting parameters to those of the viscoelastic model. Our work represents a first step towards a molecular-to-continuum methodology for the simulation of industrially relevant non-isothermal flows to predict flow characteristics and the material final properties after processing.

Thursday 11:40 Plaza I

PM33

**Interplay between dynamics and structure in microphase separated bottlebrush block copolymers with asymmetric molecular shape**Benjamin M. Yavitt<sup>1</sup>, H. Henning Winter<sup>2</sup>, and James J. Watkins<sup>1</sup><sup>1</sup>*Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States;* <sup>2</sup>*Chemical Engineering, Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

Bottlebrush Block Copolymers (BBCP) are molecules with two discrete sections, each having their own type of polymeric side chains densely grafted to the molecular backbone. Extended backbone conformations and repulsion between grafted side chains suppress chain entanglements. As a result, BBCP can rapidly self-assemble into diverse microphase separated morphologies. A comprehensive understanding of the interplay between dynamic behavior and microstructure is crucial for the implementation of BBCPs in industrial processing, such as in flow induced ordering or roll-to-roll processing. Here, we investigate the viscoelastic behavior of well-ordered poly(styrene)-b-poly(ethylene oxide) (PS-b-PEO) BBCPs with short side chain lengths (PS Mn = 3 kg/mol, PEO Mn = 5 kg/mol). The difference in side chain length produces an asymmetric shape mismatch between the two blocks, which directly influences the resulting morphology. Sequential relaxation transitions are observed through oscillatory shear rheology, and the scaling relationships show distinct power law behavior analogous to critical gels. The relaxation mechanisms are a consequence of the reduced entanglements and highly mobile microstructure. This study expands our understanding of the complex relationship between architecture and viscoelasticity in microphase separated BBCPs. Finally, we apply this interplay to the processing of highly oriented microstructures for various nanotechnology applications.

## Symposium PG

### Polyelectrolytes, Self-assembling Systems & Gels

Organizers: Nick Virgilio and Lilian Hsiao

Thursday 8:40 Bellaire

PG22

**Effect of confinement on the rheology of a yield-stress fluid**John R. de Bruyn and Yang Liu*Physics and Astronomy, University of Western Ontario, London, Ontario N6A 3K7, Canada*

We have studied the flow of Carbopol, a polymer microgel, confined to square microchannels with widths ranging from 451  $\mu\text{m}$  down to 54  $\mu\text{m}$ . Velocity profiles in the midplane of the channels were measured using particle image velocimetry. Carbopol is a yield-stress fluid, and the velocity profiles measured in the larger channels agreed well with simulations based on its measured bulk-scale rheology. In microchannels 150  $\mu\text{m}$  or smaller in width, however, the velocity profiles could not be fitted by a model with a finite yield stress, but instead were well-described by a power-law model with zero yield stress. We explain the vanishing of the yield stress in terms of the confinement by the microchannels of structural elements in the Carbopol.

Thursday 9:05 Bellaire

PG23

**Viscoelastic and hydrogen bonding character of supramolecular polyurethanes**Jeffrey Fedderly and Jaime Santiago*Naval Surface Warfare Center Carderock Division, West Bethesda, MD 20817, United States*

Supramolecular polyurethanes were synthesized from an isocyanate terminated 2-ureido-4(1H)-pyrimidinone (UPy) and a series of tetramethylene oxide polyols of varying molecular weight. Quadruple hydrogen bonded structures are produced from end to end interactions of the UPy functionality. The resulting associating polymers exhibit solid-like viscoelastic character. The hydrogen bonds dissociate at elevated temperatures and the materials exhibit liquid behavior. The solid associated state behavior of these materials was investigated using dynamic mechanical analysis in tension and creep in tension. The transitional nature of these materials from associated state to dissociated state and subsequent liquid behavior was investigated using parallel plate rheometry. Trends in properties based on the molecular weights of the polyols will be discussed. The nature of the hydrogen bonding transition from associated to dissociated state and subsequent kinetics back to associated state was investigated using FTIR and differential scanning calorimetry. Relationships between hydrogen bonding character and mechanical properties will be discussed.

Thursday 9:30 Bellaire

PG24

**Self-assembly of cellulose nanocrystals (CNCs) in chiral liquid-crystalline phase**Martin J. Pospisil<sup>1</sup>, Partha Saha<sup>2</sup>, Suhaib Abdulquddos<sup>1</sup>, Matthew M. Noor<sup>2</sup>, Virginia A. Davis<sup>2</sup>, and Micah J. Green<sup>1</sup><sup>1</sup>*Chemical Engineering, Texas A&M University, College Station, TX, United States;* <sup>2</sup>*Chemical Engineering, Auburn University, Auburn, AL, United States*

Self-assembly of dispersed cellulose nanocrystals (CNC) into helical liquid-crystalline microstructures were captured in post-shear relaxation experiments. To compare with the experiments, a time dependent Landau-de-Gennes model for CNC dynamics was simulated using a fully 3D finite element method to study the self-organization of the CNCs. Our study captured effects of gap confinement and chiral strength as the CNCs transitioned from their initially shear aligned state to their steady state cholesteric microstructure. Our simulation results indicate that texture uniformity decreases and defect density increases as either gap height or chiral strength is increased. We also observed the self-assembly of CNCs into dynamic banding patterns that precede steady state hierarchical structure. This work has immediate relevance in dispersion processing for thin film applications and gives new insight into self-assembly of dispersed anisotropic materials.

Thursday 10:25 Bellaire

PG25

**Probing the shear mechanical properties of graphene oxide hydrogels with tailored crosslinks for use as structural electrodes for energy storage**Smit A. Shah<sup>1</sup>, Dorsa Parviz<sup>2</sup>, Wanmei Sun<sup>1</sup>, Devon Kulhanek<sup>1</sup>, Jodie L. Lutkenhaus<sup>1</sup>, and Micah J. Green<sup>1</sup><sup>1</sup>*Chemical Engineering, Texas A&M University, College Station, TX 77840, United States;* <sup>2</sup>*Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

Graphene oxide (GO) based hydrogels made using sol-gel self-assembly approach have gained remarkable interest because of their high specific surface area and electrical conductivity. These properties make them a suitable active material for electrochemical energy storage applications. The electrical and mechanical properties of these hydrogels are influenced by the type and density of their crosslinks. However, detailed understanding of the rheology of these GO hydrogels is missing. GO hydrogels are known to comprise of physical crosslinks (p-p stacking) and chemical crosslinks (C-N-C covalent bonding). In this study, we investigate the composites of GO gel with aramid nanofibers (ANFs) with a goal to obtain improved mechanical properties (compressibility, toughness, strain to fracture) for their application as structural supercapacitor electrodes. We synthesized GO-ANF composite hydrogels with ANF content varying from 1-15 wt.% and compared their oscillatory shear rheological properties. Storage and loss modulus were found to be frequency independent, and storage modulus ( $G'$ ) was an order of magnitude higher than loss modulus ( $G''$ ), which is indicative of a robust crosslinked hydrogel. Our results will help understand the effect of ANFs as fillers on the crosslinking in GO hydrogels and evaluate their suitability for application as structural electrodes.

Thursday 10:50 Bellaire

PG26

**Determination of viscoelastic properties of polymer networks using probe rheology simulations**Rafikul Islam<sup>1</sup>, Nestor Valadez-Perez<sup>2</sup>, Tsutomu Indei<sup>3</sup>, Jay D. Schieber<sup>2</sup>, and Rajesh Khare<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, Texas Tech University, Lubbock, TX, United States;* <sup>2</sup>*Department of Chemical and Biological Engineering, Illinois Institute of Technology, Chicago, IL, United States;* <sup>3</sup>*Global Station for Soft Matter, Hokkaido University, Sapporo, Hokkaido, Japan*

The ability to determine viscoelastic moduli of polymer gels is important for many practical applications, such as tissue engineering. Previously, we showed that the probe rheology simulation technique in conjunction with continuum theory can predict viscoelastic properties of unentangled and weakly entangled polymer melts. In this study, we apply the probe rheology simulation technique to unentangled and entangled cross-linked polymer networks. Specifically, active and passive probe rheology simulations are performed on the coarse-grained models of polymer network systems of varying strand length. The inertial generalized Stokes-Einstein relation (IGSER) is used to relate the probe particle motion to viscoelastic properties of the medium. Results obtained from active and passive probe rheology simulations are compared with those obtained by non-equilibrium molecular dynamics (NEMD) simulations. Also, the probe particle motion measured in the passive rheology simulations and viscoelastic moduli obtained by probe rheology simulations are discussed in the context of interplay of probe particle size, network mesh size, and

entanglement tube diameter. Our results show that active and passive probe rheology simulations can be used in conjunction with the IGSER formalism to predict the viscoelastic properties of polymer network systems.

## Symposium SG Solids, Composites & Granular Materials

Organizers: Jonathan Seppala and Denis Rodrigue

Thursday 8:40 Post Oak

Keynote SG14

### **Real-time rheology management for the concrete industry**

Nathan Tregger

*GCP Applied Technologies, Cambridge, MA 02140, United States*

Concrete is the most widely used man-made material in the world with approximately 2 cubic meters produced per person each year [1]. Ready-mixed produced concrete represents a large percentage of this concrete manufactured. Yet, the deceptively simple act of delivering concrete to a jobsite is a constant struggle to achieve performance consistency due to the complexity of both the rheology and hydration of concrete. With the advent of sensors and IoT, the construction industry is beginning to embrace the value of information management. This talk will focus on rheology sensors and control systems mounted to ready-mix concrete trucks and their recent impacts on the concrete industry.

[1] Scrivener, K.L., John, V.M., and Gartner, E.M., "Eco-efficient cements: Potential, economically viable solutions for a low-CO<sub>2</sub>, cement based materials industry," United Nations Environment Program, 2016.

Thursday 9:05 Post Oak

SG15

### **Computational modelling of suspension flow in pipes: Application to cement based materials**

Nicos S. Martys, William L. George, Steven G. Satterfield, and Scott Z. Jones

*National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

The flow of suspensions in various pipe systems is important for a wide variety of applications such as the pumping and 3D printing of cement based materials, e.g., cement paste, mortars and concrete. Crucial to the successful flow and placement of such materials is the capability to predict and modify their rheological properties in situ as the viscosity may be time dependent. In this presentation, results of numerical simulation of the pipe-flow of dense suspensions are presented. We focus on the flow of mono size sphere suspensions where the matrix properties of the suspension studied are Newtonian, shear thinning and shear thickening. We find that the volumetric flow rate can generally be described by a simple scaling law that is based on the the matrix fluid's constitutive law. This is a consequence of the shearing action being largely controlled at the pipe wall. As seen in previous work on suspension flow with a Newtonian fluid matrix, the density of particles increases at the center of the pipe for all three cases of the matrix fluids studied due to shear induced migration effects. At volume fraction approximately 40 % and higher we see evidence of ordering. This feature is illuminated using an effective scattering algorithm. Issues related to proper experimental characterization of rheological properties for pumping and printing of cement based materials will be discussed.

Thursday 9:30 Post Oak

SG16

### **Use of a bi-fluidic, confining-fluid, pressurizable dilatometer to evaluate engineering and thermal properties of polymers and their composites**

Brendan R. Ondra and Alan J. Lesser

*Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

In a number of applications, accurate prediction of material performance requires a more thorough characterization of the material's engineering properties. In many cases, measurements of the in-plane properties are insufficient to fully evaluate all the properties necessary to predict the elastic, viscoelastic, and thermoelastic constitutive response. In this work, we use a new pressurizable dilatometer to measure bulk properties of both isotropic and anisotropic media. We will demonstrate its use in the evaluation of pressure and temperature dependent transitions as well as the bulk thermoelastic response between these transitions. We will then illustrate how these types of measurements can be done on anisotropic media (carbon fiber reinforced composites and polymer films) to evaluate their out-of-plane constitutive response when these measurements are coupled with complimentary in-plane measurements. We also detail a new bi-fluidic confining-fluid pressurizable dilatometer that was used to conduct this work. Whereas the majority of classical confining-fluid dilatometers make use of a bellows, our design concept centered around replacing the bellows with a fluid-fluid interface composed of two immiscible liquids that have different densities. This design change enables us to overcome the mechanical and operational restrictions that are inherent to the use of a bellows. For the hydraulic fluid, we selected an ionic liquid (1-ethyl-3-methylimidazolium ethyl sulfate) because ionic liquids have been shown to possess bulk properties which are superior to traditional hydraulic fluids. For the confining fluid, we selected a liquid metal, Galinstan. This liquid metal possesses the appropriate thermal and mechanical properties for this application. The temperature and pressure ranges for our dilatometer span 25C-250C and 7MPa-186MPa, respectively, and over these ranges, the rates of heating, cooling, and pressurization are well controlled. With a sample size of up to 2mL, we can detect volume changes down to 1µL.

Thursday 10:25 Post Oak

SG17

**Fatigue fingerprints via Fourier transform of the stress**Valerian Hirschberg<sup>1</sup>, Denis Rodrigue<sup>1</sup>, and Manfred Wilhelm<sup>2</sup><sup>1</sup>*Department of Chemical Engineering and CERMA, Université Laval, Quebec City, Quebec G1V 0A6, Canada;* <sup>2</sup>*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe 76128, Germany*

In this work, the stress response of mechanical fatigue on solid polystyrene (PS), polymethylmethacrylate (PMMA) and styrene-acrylonitrile (SAN) samples in oscillatory shear tests was analyzed via Fourier transform (FT) to determine fingerprints of continuous fatigue. The tests were performed at room temperature using a torsion rectangular geometry (notched rectangular samples) and filmed by a video camera to visualize changes in the samples such as crack initiation or propagation. Large strain amplitudes were applied so the stress response was nonlinear and higher harmonics detectable in the FT spectra. The analysis includes the time evolution of the stress response via linear (storage ( $G'$ ) and loss ( $G''$ ) moduli) and nonlinear (higher harmonics) parameters, as well as their time derivatives. These parameters were used to better understand and further analyze the fatigue behavior of a material and to detect/follow specific events such as crack initiation and propagation leading to fatigue lifetime prediction. The results showed that during a test, the linear parameters ( $G'$  and  $G''$ ) decreased monotonically, while the  $I_{3/1}$  intensity (relative amplitude of the third harmonic to the fundamental one) increased steadily until failure. These three parameters were found to change linearly with time (number of cycles) over a specific time frame, shortly after the beginning of the test. The fatigue lifetime was found to follow a power-law function of the (time dependent) rates of change (slopes) of  $G'$ ,  $G''$  and  $I_{3/1}$  in this regime. For undamaged samples, the nonlinear parameter  $I_{2/1}$  (relative amplitude of the second harmonic to the fundamental one) is within the noise level, but its intensity increased when (visible) defects are created (macroscopic cracks). The time evolution of  $G'$ ,  $G''$ ,  $I_{3/1}$  and  $I_{2/1}$  are proposed as new criteria to predict failure and detect the onset of macroscopic cracks under the conditions tested, to better determine safety limits (partial damage).

**Symposium ET****Advanced Experimental Techniques/Methods in Rheology**

Organizers: Kalman Migler and Simon Rogers

Thursday 8:40 San Felipe Room

ET27

**Planar Couette flow for magnetic resonance microscopy**Sarah J. Stevenson, Timothy I. Brox, and Petrik Galvosas*Victoria University of Wellington, Wellington, New Zealand*

Rheo-NMR is a technique to study complex material responses to mechanical deformation by combining methodologies from rheometry and nuclear magnetic resonance (NMR) [1]. Through the manipulation of nuclear spins, NMR may be used to observe local mechanical phenomena or probe the molecular origins for these behaviours. It does this without the need for tracer or scattering particles, or a transparent sample, with the flexibility of full 3D spatial mapping and velocity encoding in any direction.

Here we report on a novel geometry for Rheo-NMR, a planar-cylindrical hybrid (PCH) shear cell which includes planar regions to generate simple shear. Similar devices have been used to study the fluid mechanics of simple fluids [2] but have never been developed for NMR. They are composed of two parallel sections of planar flow connected by two sections of semi-circular flow to give a closed flow path in the shape of a racetrack. Shear is applied by rotating a band around the inner section like a conveyor belt. The goal of the PCH geometry is to eliminate the stress variation found in a concentric cylinder / Taylor-Couette (TC) cell. Previous work with a 10% CPCI / NaSal (2:1) in 0.5M NaCl wormlike micelle (WLM) solution demonstrated that the curvature of TC cells used during Rheo-NMR experiments influenced the onset of shear banding [3].

Using the PCH we further investigated the influence of stress variation on the WLM solution mentioned above with advanced NMR velocimetry [4]. When compared to a Newtonian fluid the WLM solution still revealed itself as a non-Newtonian material. However, no signature of shear banding occurred neither in the planar nor in the circular sections of the flow field, a result calling for further research.

[1] P.T. Callaghan, Rep. Prog. Phys. 62, 599-670 (1999). [2] J.J. Koblitz and T. Mullin, Phys. Fluids 13, 1583-1593 (2001). [3] T.I. Brox et al., J. Rheol. 60, 973-982 (2016). [4] S. Kuczera and P. Galvosas, J. Magn. Reson. 259, 135-145 (2015).

Thursday 9:05 San Felipe Room

ET28

**Polymer degradation in cone-plate rheometry**Peter H. Gilbert and Alan J. Giacomin*Chemical Engineering, Queen's University, Kingston, ON K7L 3N6, Canada*

We analyze quantitatively the oxidative degradation of a polymer sample in a cone-plate rheometer. We consider the sample degradation caused by oxygen diffusing from the sample boundary to its interior. We examine rheometer error mitigation by means of nitrogen blanketing, and also, of cone-plate partitioning. We arrive at exact analytical expressions for the oxygen concentration, and thus, for the degradation rate. We then integrate this over time to get the amount of oxygen reacted as a function of radial position and time, in the degrading sample.

Thursday 9:30 San Felipe Room

ET29

**Observation of semiflexible filament thermal bending and transport in complex porous media**Zhao Tang, Shannon Eichmann, Fred C. MacKintosh, and Matteo Pasquali*Department of Chemical & Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Extracting high-resolution shape and position information of semiflexible filaments in different media from thousands of noisy microscopy images is the basis for understanding their mechanical and transport properties. Recent automated image processing algorithms yield subpixel resolution of the filament backbone shape in free medium via a piece-wise Gaussian-fit on pixel intensities. These algorithms yield the trajectories, orientation and bending mode amplitudes, which in turn can be used to determine mean square displacement (MSD) and mean square angular displacement (MSAD). These latter quantities relate to translational and rotational diffusivity and persistence length. However, the accuracy of the MSD and MSAD are limited by optical resolution, pixilation, and time-resolution; additional diffraction can occur in complex inhomogeneous media. Here we obtain higher resolution single-walled carbon nanotube (SWCNT) backbone points from near infrared microscopy videos of SWCNTs in porous media by further improving pixel intensity sampling method by nearby pixels interpolation. Moreover, we quantify the static error in MSDs from immobile filaments at different noise levels, and we extend dynamic error estimation from spherical particles to thread-like molecules. We apply this method to study the dynamics of highly confined stiff filaments (~10  $\mu\text{m}$  in length) in uniformly sized colloidal packing pores a few hundred nanometers in size. We find several translation and rotation Brownian dynamics regimes due to pore structure heterogeneity. Additionally we find that, in straight pores, filament bending energy decreases due to pore confinement; bending energy increases when a filament has to navigate across pores with different orientation, i.e., diffusion must occur against a gradient of elastic energy as a filament changes orientation across pores. This innovative imaging processing algorithm and its results are crucial to understanding filament mechanical and transport properties in emerging systems.

Thursday 10:25 San Felipe Room

ET30

**Methods to characterize microstructural transitions in suspensions**Sebastian Bindgen<sup>1</sup>, Frank Bossler<sup>2</sup>, Joost de Graaf<sup>3</sup>, and Erin Koos<sup>1</sup>*<sup>1</sup>Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium; <sup>2</sup>Institute for Mechanical Process Engineering, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany; <sup>3</sup>Institute for Theoretical Physics, Utrecht University, Utrecht 3584 CC, The Netherlands*

Suspensions can exhibit a wide range of rheological behaviors such as shear thinning, shear thickening, and normal stress differences. These behaviors are closely linked to both the bulk particle structure as well as the microstructure including direct particle contacts. Traditionally, localized parameters such as the coordination number and pair correlation function as well as larger scale measures such as the average floc size and fractal dimensionality have been used to analyze the structure of these materials. While these parameters can correlate to the measured rheological response, their application is often of limited use, e.g. fractal dimension for sparse networks. Graph theory offers other methods and parameters that can be used to analyze complex structures. This effort is aided by advances in confocal microscopy and computational simulations where direct information about the particle positions and bond strength are accessible.

This method is primarily demonstrated using ternary liquid-liquid-solid systems [1], which exhibit a wide variety of different morphologies depending on the ratio of the three components. As the volume ratio of secondary fluid to particles  $\phi_{\text{sec}}/\phi_{\text{solid}}$  is changed, a transition from a granular system without added liquid, through a sparser capillary suspension network at intermediate volume ratios, to a network of dense aggregates at larger ratios is observed. This analysis technique is also demonstrated for a computational simulation of a sedimenting colloidal gel. We analyze these networks using the coordination number and clustering coefficient. The clustering coefficient is a measure of the clique-iness of a network and should correspond to the rigidity of these structures, whereas the coordination number just counts the number of neighbors regardless of their configuration. These parameters are compared to the measured storage and loss moduli.

E. Koos and N. Willenbacher. *Science*, 331(6019), 897-900.

Thursday 10:50 San Felipe Room

ET31

**Probing the rheological properties of natural and synthetic fibers with a simple torsional pendulum**Bavand Keshavarz<sup>1</sup>, Brady Zarket<sup>2</sup>, Gareth H. McKinley<sup>3</sup>, and Niels Holten-Andersen<sup>1</sup>*<sup>1</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States; <sup>2</sup>Advanced Research, L'Oréal, Clark, NJ 07066, United States; <sup>3</sup>Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Understanding the mechanical properties of natural and synthetic fibers is of great importance in many biological and industrial applications. Microscopic techniques such as micro/nano indentation already exist but these tests are often hard to perform and there are certain limitations in macroscopic interpretations of the obtained results. We explore the properties of a series of natural and synthetic fibers, with a simple torsional pendulum. The torsional oscillation of the mass-fiber system is precisely recorded with an HD video-camera and an image processing algorithm is used to analyze the resulting videos. Analysis of the processed images show a clear damped oscillatory response and a simple mechanical model can describe the amplitude decay of the oscillation data very well. The natural frequency of the oscillation and the corresponding damping ratio can be extracted using a logarithmic decrement method and directly connected to the bulk viscoelastic properties of the fiber plus any surface coating or 'sizing' that might be applied. We further study the sensitivity of these measurements to the chemo-mechanical properties of the outer layers of the fiber structure at different levels of humidity and pH. A parallel series of tests are performed on a strain-controlled rheometer in both torsional and elongational deformation modes. Results from this study can help us understand the effects of chemistry and microstructure on mediating the final mechanical properties of natural/industrial fibers.

## Symposium FE Foams, Emulsions & Interfacial Rheology

Organizers: John Frostad and Joseph Samaniuk

Thursday 8:40 Tanglewood

FE18

### **Dynamics of stratification in micellar freestanding films**

Yiran Zhang, Subinuer Yilixiati, Chenxian Xu, and Vivek Sharma

*Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

Ultrathin films exhibit stratification due to confinement-induced structuring and layering of small molecules in simple fluids, and of supramolecular structures like micelles, lipid layers and nanoparticles in complex fluids. Stratification proceeds by the formation and growth of thinner domains at the expense of surrounding thicker film, and flows and instabilities drive the formation of nanoscopic terraces, ridges and mesas within a film. The detailed mechanisms underlying stratification are still under debate, and are resolved in this contribution by addressing long-standing experimental and theoretical challenges. Thickness variations in stratifying films are visualized and analyzed using interferometry, digital imaging and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). Using IDIOM protocols we developed recently, we characterize the shape and the growth dynamics of nanoridges and mesas that flank the expanding domains in micellar thin films. We show that topographical changes including ridge growth and instability, and the overall stratification dynamics, can be described quantitatively by nonlinear thin film equation, amended with supramolecular oscillatory surface forces.

Thursday 9:05 Tanglewood

FE19

### **Dynamics of bubble-bubble pinch-off in a microfluidic expansion channel for high throughput foam generation**

Daniel J. Vecchiolla, Vidya Giri, and Sibani Lisa Biswal

*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Paramount to the optimal design of foam generation systems is the understanding of the complex dynamic interactions that govern bubble breakup. Recent experimental work has demonstrated that close confinement of bubbles can facilitate neighbor-neighbor bubble pinch-off, where the strong interactions of two or more bubbles break a central elongated bubble. This “structure-induced capillary instability” elucidated the process of bubble breakup in sheared foams and manifested in the discovery of two fundamental pore-level mechanisms of foam generation in porous media. The present work offers a novel microfluidic foam generation system for production of ordered, bi- or tridisperse foams at capacities exceeding 10,000 daughter bubbles per second. Bubble-bubble pinch-off occurs near the entrance of the expansion region of a wide 1600  $\mu\text{m}$  collection channel. Pinch-off is systematic at sufficiently large strain rates, assisted by a clear templating effect from the bubbles in the expansion. The relationship between the capillary number, the upstream shear rate, and the size distribution of fragmented bubbles is examined. The banded size segregation of fragmented and intact bubbles is primarily governed by the channel geometry, and the foams remain ordered as they flow through the collection channel. The mechanism of bubble-bubble pinch-off in an expansion differs from the corresponding neighbor-neighbor pinch-off phenomenon discovered in pore constriction studies. The use of bubble-bubble pinch-off for tridisperse foam generation allows for the fluidic resistance to be adjusted to access a spectrum of bubble size ratios for a fixed expansion wall geometry. The simplicity in operating and characterizing our system will broaden microfluidic foam research by enabling studies on dynamic bubble interactions and higher complexity foam flows.

Thursday 9:30 Tanglewood

FE20

### **Foamability of aqueous solutions of charged surfactants and of surfactant-polymer mixtures**

Carina Martinez, Camila U. Ortiz, and Vivek Sharma

*Chemical Engineering, University of Illinois at Chicago, Chicago, IL, United States*

The stability of a freshly created foam is intimately linked with the rate of mass transfer of a surfactant from liquid sub-phase to the interface, and this diffusion- or adsorption-limited kinetics is said to impact the so-called foamability. Dynamic surface tension refers to the time dependent variation in surface tension, and is intimately linked with the rate of mass transfer of a surfactant from liquid sub-phase to the interface. Dynamic surface tension measurements carried out with conventional methods like pendant drop analysis, Wilhelmy plate, etc. are limited in their temporal resolution (> 50 ms). In this study, we describe design and application of maximum bubble pressure tensiometry for the measurement of dynamic surface tension effects at extremely short (1-50 ms) timescales. Using experiments and theory, we discuss the overall adsorption kinetics of charged surfactants, paying special attention to the influence of added salt on dynamic surface tension. We show that the pinch-off dynamics of bubbles plays an important role in determining the accuracy of dynamic surface tension measurements. Finally, we examine how bubble formation and pinch-off dynamics as well as dynamic adsorption are modified in the presence of added polymers by including a critical examination of extensional rheology effects.



Thursday 10:25 Tanglewood

FE21

**Developing conducting immiscible PP/PS blends with a percolated polyaniline/PA filler by tuning their specific interactions with the compatibilizer**Prakhyat Hejmady<sup>1</sup>, Avanish Bharati<sup>2</sup>, Ruth Cardinaels<sup>1</sup>, and Paula Moldenaers<sup>2</sup><sup>1</sup>*Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands;* <sup>2</sup>*Department of Chemical Engineering, KU Leuven, Leuven, Belgium*

We have investigated the effect of master batch preparation techniques such as by extrusion and solution casting to develop a double-percolated network of conducting Polyaniline (PANI) in immiscible PP/PS blends. The strategy adopted to develop conducting blends was to concomitantly drive the morphology of the immiscible blend to a cocontinuous structure and control the localization of the PANI using specific interactions with an interfacially segregated SEBS-g-MA compatibilizer. A percolated composite of PANI in Polyamide (PA) is used as the conducting filler, and we envisage that the hydrogen bonding of PA with MA of the copolymer drives the localization of the PANI to the copolymer. Hence, master batches of the conducting PANI and copolymer with increasing PANI concentration were prepared by extrusion and solution casting. The master batches were subsequently added to the polymer constituents (PS or PP/PS) using different sequences of solution and melt mixing to localize the PANI either in the polar PS phase or partially at the interphase. The thus prepared blends led to a synergistic increase in the conductivity (6 decades) and dynamic moduli with increasing PANI and copolymer concentrations, whose effect was investigated for various blend compositions. Our findings were warranted by STEM micrographs, in which for blends with solution casted master batches, PANI-PA selectively localized at the interphase or in the minority matrix phase of the PP/PS blend. The latter was attained due to phase inversion with increased copolymer concentration. In addition, we established the essential role of interactions between the conductive PANI-PA composite and the MA functionality of the SEBS-g-MA in the localization process. In summary, various master batch techniques were employed to optimize the percolation of the conductive polymer PANI in PP/PS blends, allowing to generate easily processable conductive PP-PS blends.

Thursday 10:50 Tanglewood

FE22

**Tuning the phase separated morphology by developing self-compatibilizing polymer blends**Avanish Bharati<sup>1</sup>, Jens Allard<sup>1</sup>, Ruth Cardinaels<sup>2</sup>, and Paula Moldenaers<sup>1</sup><sup>1</sup>*Department of Chemical Engineering, KU Leuven, Leuven B-3001, Belgium;* <sup>2</sup>*Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands*

A bi-phasic P $\alpha$ MSAN/PMMA blend undergoing spinodal decomposition was compatibilized with short unentangled PS polymers. This self-compatibilization was compared with that by unentangled PS-b-PMMA block copolymers. The compatibilization effectiveness of the PS polymers and the block copolymers was assessed by in-situ characterization of the matrix-droplet morphology as well as the small-amplitude dynamic moduli as a function of coalescence time using a flow-induced coalescence protocol. The effectiveness was demonstrated by their ability to segregate to the blend's interface, established from the decrease in the interfacial tension and coalescence suppression of the PMMA droplets in 85/15 P $\alpha$ MSAN/PMMA blends. The effects of the compatibilizers on the phase separation thermodynamics and kinetics were investigated for 85/15 and 40/60 blends, exhibiting droplet-matrix and co-continuous morphology, respectively. Thermodynamically driven phase separation was monitored using small amplitude oscillatory shear (SAOS) measurements during temperature sweeps. The critical temperature was reduced by  $\sim 8^\circ\text{C}$  upon compatibilization. The kinetics of phase separation, monitored at equal quench depths by performing SAOS measurements, was substantially slowed down due to twofold activity of the compatibilizer. Their rapid diffusion was mediated by enthalpic interactions resulting in interfacial segregation. The diffusion time obtained from the inverse Laplace transformation (ILT) of the time evolution of the dynamic moduli was in agreement with the Rouse dynamics. Subsequent compatibilization resulted in interfacial tension mediated suppression of coarsening of the P $\alpha$ MSAN domains in 40/60 blends. This resulted in substantial morphology refinement and increased the degree of co-continuity of the P $\alpha$ MSAN phase, as confirmed by relaxation spectra of the SAOS response and optical microscopy. Our highly robust novel polymers for self-compatibilization thus uniquely allow tuning the phase-separated morphology.

Thursday 11:15 Tanglewood

FE23

**Modeling the viscoelastic properties of mesophases using intermicellar interactions**

Sahar Qavi and Reza Foudazi

*Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

Amphiphilic block copolymers self-assemble at water/oil interface and form different mesomorphic structures, such as lamellar, micellar cubic, normal hexagonal and reverse hexagonal structures. While the elasticity of the single crystal of these mesophases depends on the orientation, their elastic properties are isotropic due to the polycrystalline structure. In this work, we provide a model to predict the elasticity of mesophases from their characteristic length and intermicellar interactions. Rheological properties of different mesophases of Pluronics in the presence of water and p-xylene are used as case study. Micellar cubic structures have the highest value of elasticity. Normal hexagonal mesophases have higher elasticity compared to reverse system due to the difference in the continuous phase and lattice parameter. Lamellar mesophases show at least one order of magnitude lower elasticity compared to the other systems due to the sliding of the planes in two directions. In the studied frequency range, lamellar and hexagonal mesophases show two distinct relaxation times.

## Symposium NF Non-Newtonian Fluid Mechanics & Flow Instabilities

Organizers: Aditya Khair and Christian Clasen

Thursday 8:40 Plaza II

NF27

### **Extensional rheology: A microstructural probing technique for living polymers**

Rose Omidvar and Hadi Mohammadigoushki

*Chemical Engineering, Florida State University, Tallahassee, FL 32310, United States*

We used capillary break-up extensional rheometer (CaBER) and dripping on a substrate (DoS) techniques to study two series of wormlike micelle solutions; sodium oleate/octyl trimethylammonium bromide (NaOA/OTAB) and Cetylpyridinium chloride/Sodium salicylate (CPyCL/NaSal). These systems show a peak in zero shear viscosity or shear relaxation time beyond a critical salt to surfactant ratio. Cryo-TEM images have indicated that system based on NaOA/OTAB experiences a transition from linear to shorter linear micelles beyond this maximum. However, linear wormlike micelles based on CPyCL/NaSal become branched beyond the viscosity peak. In this study, we investigated whether different microstructural transitions can be distinguished via extensional techniques. Our results indicate that for most of extensional parameters, these systems behave similarly. However, we report some differences in behavior of filament life time in these two systems with both techniques. Finally, we will show that DoS experiments with wormlike micelles needs special care to prevent wetting effect.

Thursday 9:05 Plaza II

NF28

### **On the measurement and characterization of velocity-slip in Couette-rheology of viscoelastic fluids**

Martin N. Azese

*Mechanical Engineering, Texas Tech University, Lubbock, Texas, TX 79409, United States*

We present a robust calculation that leads to an experimentally convenient way of measuring and characterizing velocity slippage involved in the dynamics of viscoelastic fluids. In the analysis, unsteady Navier-Stokes equation coupled with linear viscoelastic model-equation is solved while highlighting the rheological ramification. This approach is similar to that done in an earlier paper by the same author (M. N. Azese: Physics of Fluids, 2018)<sup>(1)</sup>, where instead it was a Newtonian Fluid. Accordingly, the sample fluid is trapped in the gap between two parallel plates (Couette), where one of them is stationary, meanwhile the other is oscillating steadily with a prescribed amplitude ( $Re$ =Reynolds number) and a prescribed angular speed of ( $\Omega=Ro$ =Roshko number), thus Couette-rheometry.

In this presentation, we also showcase an alternative way of obtaining the steady-periodic solution which is analogous to the long-time solution obtained in (1). This alternative method requires a meticulous recognition and construction of Eigen-solutions in such way as to infer temporal condition while only revealing the boundary conditions. Although we obtain the unsteady solution for this viscoelastic case, we also use the alternative method to obtain the steady-periodic solution, which we use to obtain the velocity and stress at the walls. Interestingly, we note the influence of  $Re$ ,  $Ro$ , and  $Wi$  (Weissenberg number) on this analysis. The equations and the subsequent plots that we present show the influence of slip, and we conclude that with a well-constructed inverse routine, the slip parameters can be re-produced leading to a systematic measurement and characterization of slip, useful in the calibration of readings in rheological devices.

Thursday 9:30 Plaza II

NF29

### **Next-generation aerosol technology for viscoelastic fluids: Filament Extension Atomization**

Jerome Unidad, Ravi Neelakantan, and David Johnson

*Hardware Systems Laboratory, PARC, A Xerox Company, Palo Alto, CA 94304, United States*

PARC is developing a next-generation aerosol technology that can generate droplets (mist) from viscoelastic fluids based on a roll-to-roll process that heavily involves fluid extension. While conventional spray methods tend to be viscosity-limited and do not perform reliably for strain hardening fluids, PARC's technology called Filament Extension Atomization TM (FEA) can generate high-quality narrowly-dispersed micron-sized droplets exactly from these strain hardening fluids. These could range from polymer solutions, polymer melts and other systems that exhibit extensional hardening. In this contribution, we will present a systematic mapping of the spray quality (particle size distribution, particle velocity distribution) generated by FEA as determined by processing parameters from a series of strain hardening polymer solutions with concentrations spanning the dilute, semi-dilute and concentrated regimes. We will discuss the role of strain hardening and fluid extensional behavior on spray processing through FEA and in the resulting spray quality. Some compelling use cases in additive manufacturing and in biomedical and biotechnological applications will also be discussed.

Thursday 10:25 Plaza II

NF30

### **3D finite element method for predicting extrudate swell of domains containing sharp corners**

Michelle M. Spanjaards, Martien A. Hulsen, and Patrick D. Anderson

*Mechanical Engineering, Polymer Technology Group, Eindhoven University of Technology, Eindhoven, Noord-Brabant 5600 MB, The Netherlands*

Extrusion is a widely used process to create products with a fixed cross-sectional profile. Many applications require cross-sections of complex shapes, containing sharp corners. Common requirement on the extrudate is dimensional precision. The dimensions of the extrudate, however, are

highly influenced by a phenomenon called extrudate swelling, where the extrudate will start to expand due to internal stresses once it leaves the die. When the extrudate has such a shape that it contains sharp corners, the material lines exiting from the corners will swell in two directions. Also, the sharp kink in the surface will be maintained over a large distance from the exit of the die.

We developed a computational model, using the finite element method, to predict extrudate swelling for extrudates containing sharp corners. This model describes the corner lines of the domain separately to obtain the positions of these lines in the two swell directions. A 2D height function is used to describe the free surfaces of the extrudate [1], using the positions obtained from solving the material lines to expand the domain of the height function. First a cylindrical die is modelled, where the cylindrical extrudate contains four swell surfaces and therefore also four 'corner' lines. The swell results are compared to a 2D axisymmetric model of the same problem to validate the code. In this talk we will show that the model is applicable to a wide variety of die shapes by showing swell results of different extrudate geometries of increasing complexity. The next step is to find the influence of different constitutive models and non-linear rheological parameters on the swell of extrudates of these complex shapes, so that we can predict and tune the final dimensions of the product. We hope to present some first results of this at the meeting.

References: [1] Keunings, R. An Algorithm for the Simulation of Transient Flows with Free Surfaces *Journal of Computational Physics* 199:220-62 1986.

Thursday 10:50 Plaza II

NF31

### **Pressure loss and flow behavior of gels over a constriction in a pressure driven flow**

Alexander D. Stiefel<sup>1</sup>, Christoph U. Kirchberger<sup>1</sup>, Helmut K. Ciezki<sup>1</sup>, and Guido Kurth<sup>2</sup>

<sup>1</sup>*Institute of Space Propulsion, DLR German Aerospace Center, Hardthausen 74239, Germany;* <sup>2</sup>*Bayern-Chemie GmbH, Aschau am Inn 84544, Germany*

Gels have properties which are advantageous for numerous applications; one of these applications is the use of gels as rocket propellants. Due to the partly solid, partly liquid behavior, gels combine the advantages of solid and liquid propellants. They can be handled more easily than liquids, yet a gel rocket motor with variable thrust can easily be realized, unlike with solid propellants. Furthermore, by adding additives to the gel, the propellants properties can be modified. Therefore the flow behavior of gels is of interest and is examined in, as a simplification of more complex geometries in the feeding system, a constriction. Because of the advantageous properties and the non-Newtonian properties flow and pressure loss examinations are performed. Serving as a simplification for the more complex geometries in the feeding system, the geometry of interest is a pipe with a constriction. Pipes with different area ratios are deployed but all with the same diameter upstream of the constriction. The gels used in this work are viscoelastic and pseudo-plastic fluids. Furthermore, they are thixotropic, and the reduction in the viscosity and the liquefaction are reversible. Besides the pressure loss, which was measured, the pressure loss coefficient and the generalized Reynolds number according to the extended Hershel Bulkley model are calculated analyzed. The major properties of gels which are shear thinning behavior and pseudo plasticity are reflected. The pseudo-plasticity leads to a convergence of the pressure losses of gels and Newtonian fluid for higher velocities. The yield stress causes a pressure loss already at a velocity of 0 m/s which means that a certain pressure is required for the gel to start flowing. Further, optical methods were used to make the flow field around the constriction visible and examine the velocity profile upstream and downstream of the constriction. This gives a deeper insight in the flow than only pressure measurement would do.

Thursday 11:15 Plaza II

NF32

### **Applicability of the von Mises criterion to soft solids**

Paulo R. de Souza Mendes<sup>1</sup>, Luiz Sica<sup>1</sup>, and Roney L. Thompson<sup>2</sup>

<sup>1</sup>*Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, RJ, RJ 22451900, Brazil;*

<sup>2</sup>*Mechanical Engineering, UFRJ, Rio de Janeiro, Brazil*

A constitutive model that is capable of predicting the mechanical behavior of viscoplastic materials is needed in numerical solutions of complex flows of these materials. The constitutive equation most commonly employed is the generalized Newtonian fluid model in conjunction with a Bingham or Herschel-Bulkley viscosity function, but, when elasticity is important, elasto-viscoplastic models are also used. Embedded in all these constitutive equations is the von Mises criterion. This criterion compares the intensity of the deviatoric stress---i.e. the square root of half its second invariant---to a single scalar, namely the so-called yield stress. Therefore, the yield stress should be the same regardless of the flow type employed in its measurement. We determined the yield stress of six different soft solids, based on measurements in shear flow, traction flow and compression flow. Our results revealed enormous discrepancies between the yield stress values obtained with the different flows, indicating that the von Mises criterion is not applicable to the materials investigated.

Thursday 11:40 Plaza II

NF33

### **Numerical simulations of particulate fouling in microchannels**

Marco Trofa, Gaetano D'Avino, Giovanna Tomaiuolo, Francesco Greco, Pier Luca Maffettone, and Stefano Guido

*Università di Napoli Federico II, Naples, Italy*

The development of micro and nanotechnologies has provided the possibility of synthesizing, analyzing, and manipulating particles with micrometric and submicrometric characteristic dimensions under continuous flow conditions. In many systems, the suspended particles show adhesive properties leading to undesired phenomena such as fouling and clogging. Fouling is the continuous deposition of particles on an initially clean surface, whereas clogging is the mechanism that interrupts the transport of particles in confined geometries. Although these phenomena have been thoroughly studied, the complete mechanism is far from being fully understood. In this work, we study the initial growth of an aggregate at the wall of a slit microchannel by using Computational Fluid Dynamics (CFD) combined with the Discrete Element Method (DEM). We

consider a suspension of 'soft' micro particles in a Newtonian liquid, with a simple model to describe particle-particle adhesion. The parameters considered in the simulations are taken from our recent experimental study on cluster growth in a microreactor. The results are presented in terms of cluster morphology and growth rate, quantified by the projected area onto the slit wall. A reasonable agreement with experimental data is found.

## Poster Session

### Symposium PO Poster Session

Organizers: Vivek Narsimhan and Rajesh Khare

Wednesday 6:30 Woodway II/III

PO1

#### **The impact of elevated pressure on surfactant transport to fluid-fluid interfaces**

Zachary R. Hinton and Nicolas J. Alvarez

*Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States*

Surfactants are critical to processes involving elevated pressure from oil recovery to industrial cleaning. Very little experimental exploration of the impact of pressure on surfactant interfacial phenomena exists leading to a general lack of understanding of fundamental surfactant behavior. In this work we use a novel high pressure microtensiometer to measure surfactant transport to the water-CO<sub>2</sub> interface. From experimental measurements we show that pressure has a pronounced effect on surfactant isotherms and surfactant efficacy. Additionally, we show the role of pressure on dynamic interfacial tension and interfacial rheology. Through this work we broaden the understanding of dynamic surfactant processes at elevated pressures allowing improved design of existing and novel processes.

Wednesday 6:30 Woodway II/III

PO2

#### **pH-responsive Pickering emulsions stabilized by nanoparticles-polyelectrolytes complexes**

Shumaila Shahid, Swaroop R. Gurram, and Madivala G. Basavaraj

*Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India*

There is a growing interest in the design of stimuli-responsive Pickering emulsions wherein their formation and destabilization can be controlled by changing pH, temperature or any external field. Such emulsions can be exploited for applications in various fields such as oil recovery, emulsion polymerization, pharmaceuticals, etc. In the present work a simple approach to prepare highly stable pH-responsive Pickering emulsion from mixtures of commercially available oppositely charged nanoparticle and polyelectrolyte is proposed. We demonstrate that the hetero-aggregation of oppositely charged nanoparticles and polyelectrolytes can be exploited to formulate emulsions with long term stability of more than 8 months. The particle polyelectrolyte complex formation is observed due to hetero-aggregation of oppositely charged Ludox CL nanoparticles and poly(4-styrenesulfonate) sodium salt (PSS) when dispersed in aqueous solution at pH 2-11. These complexes readily adsorbed to the oil-water interface and thus stabilize oil-in-water Pickering emulsions. The influence of various parameters such as mixing fraction, pH, energy input on the formation of Pickering emulsions, comprehensive analysis of the combined effect of both pH and mixing fraction on the droplets size and also the aggregation behaviour of nanoparticle - polyelectrolyte mixtures will be presented. The emulsions formed are observed to be doubly pH responsive. We show that the aggregation of oppositely charged species that stabilize emulsions can be tuned such that destabilization of emulsions can be readily controlled. This is achieved by adjusting the pH of the continuous phase either by the addition of an acid or a base and thus provides a convenient handle to control the stability of emulsions.

Wednesday 6:30 Woodway II/III

PO3

#### **Rhamnolipids formulation design: A microrheological study**

Liangchen Xu, Yao Zhou, and Samiul Amin

*Chemical Engineering, Manhattan College, Bronx, NY 10463, United States*

The global surfactant market is expected to reach \$44.9 billion by 2022, of which 67% of the demand is from the personal care and detergents market [1]. Due to consumers' increasing awareness on product sustainability, the microbially produced biosurfactants are increasingly gaining the interest of the personal care industry as potential alternatives for traditional petroleum derived and chemically synthesized surfactants [2]. The future of personal care and detergent products is the elimination of non-biodegradable, environmentally toxic surfactants. However, prior to that, an understanding of how performance criteria such as rheology is affected by substitution of traditional surfactants with biosurfactants is required. In this study, the effect of rhamnolipid biosurfactant on the rheological response of traditional surfactants such as sodium laureth sulfate and cocamidopropyl betaine is explored utilizing mechanical rheometry, optical microrheometry, and microfluidic rheometry. The study provides unique insights into microstructure-rheology-tribology linkages in complex biosurfactant-surfactant mixtures.

Reference [1] News & Views - Market Reports: Global Markets for Surfactant Chemicals and Materials. Chemical Industry Digest. 2018. ISSN: 0971-5266. [2] Fakruddin Md (2012) Biosurfactant: Production and Application. J Pet Environ Biotechnol 3:124. doi:10.4172/2157-7463.1000124

Wednesday 6:30 Woodway II/III

PO4

**Effect of rhamnolipid biosurfactant on surface tension and interfacial rheological behavior with SLES/CAPB surfactant system**Yao Zhou, Liangchen Xu, and Samiul Amin*Chemical Engineering, Manhattan College, Bronx, NY 10463, United States*

The global surfactant market is expected to reach \$44.9 billion by 2022, of which 67% of the demand is from the personal care and detergents market [1]. Due to consumers' increasing awareness on product sustainability, the microbial-produced biosurfactants are increasingly gaining the interest of the personal care industry as potential alternatives for traditional petroleum-derived and chemically synthesized surfactants [2]. The future of personal care and detergent products is the elimination of non-biodegradable, environmentally toxic surfactants. However, prior to that, an understanding of performance criteria such as surface tension is affected by substitution of traditional surfactants with biosurfactants is required. This study mainly focuses on the influences of rhamnolipid biosurfactant on surface tension and interfacial tension of sodium laureth sulfate and cocamidopropyl betaine. Furthermore, the effect of rhamnolipid on interfacial rheological responses with different oils in the surfactant mixture are also characterized.

Reference: [1] News & Views - Market Reports: Global Markets for Surfactant Chemicals and Materials. Chemical Industry Digest. 2018. ISSN: 0971-5266 [2] Fakruddin Md (2012) Biosurfactant: Production and Application. J Pet Environ Biotechnol 3:124. doi:10.4172/2157-7463.1000124

Wednesday 6:30 Woodway II/III

PO5

**Interfacial dilatational rheology and the controlled fabrication of surfactant- and particle-stabilized emulsions**Jerome J. Nash and Kendra Erk*School of Materials Engineering, Purdue University, West Lafayette, IN 47907, United States*

Fluid interfaces containing surfactants and particles have rheological properties that are vital to the anticipated bulk kinetic stability of emulsions. Many practical applications of emulsions necessitate high kinetic stability during storage, while in other cases, separation-resistant emulsions are entirely unwanted. Innovative techniques for controlling emulsion phase separation processes, which are largely governed by the rheology of interfacially-adsorbed species, are highly desired. Yet, the utility of these techniques is often limited by difficulties with measuring and interpreting the rheological properties of complex fluid interfaces, leaving open questions about the relationship between interfacial rheology and bulk emulsion stability. Thus, this contribution presents three fundamental investigations that provide compelling insights on the complex interplay between the interfacial dilatational rheology of oil-water interfaces in the presence of surfactants and/or particles and the observed resistance of bulk oil-in-water emulsions to coalescence and kinetic destabilization. The interfacial dilatational rheology of fluid interfaces in the presence of adsorbed emulsifiers was probed via drop shape analysis and bulk emulsion stability was characterized using optical microscopy, photon correlation spectroscopy, and visual observation. The dilatational elastic modulus of adsorbed interfacial layers was shown to correlate closely to the bulk release profile of active payload-containing nanoemulsions and the onset of coalescence between neighboring emulsion drops with surfactant- or particle-laden interfaces, where emulsions with more elastic interfaces displayed both retarded payload release and improved resistance to droplet coalescence. The knowledge garnered from these studies is highly relevant to academic and industrial emulsion formulators who seek inexpensive, yet robust methods for predicting, characterizing and customizing the kinetic stability of emulsified systems.

Wednesday 6:30 Woodway II/III

PO6

**Characterizing rheological and interfacial properties of asphaltenes in the presence of chemical dispersants**Yu-Jiun Lin<sup>1</sup>, Gordon F. Christopher<sup>2</sup>, and Sibani Lisa Biswal<sup>3</sup>*<sup>1</sup>Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United States; <sup>2</sup>Texas Tech Univ, Lubbock, TX 79423, United States; <sup>3</sup>Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Asphaltene are components in crude oil known to deposit and stabilizing emulsions interrupting flows in critical regions during oil production. Chemical dispersants are commonly used to disperse asphaltene into smaller agglomerates or increase asphaltene stability in solution with the goal of preventing adsorption. However, in many cases, these chemical dispersants fail in the field or even worsen the problems in the wellbores. Further understanding of the mechanisms by which dispersants alter rheological and interfacial properties of asphaltene is needed. Here, we describe the use of porous media microfluidic devices and a modified rheometer to evaluate how chemical dispersants change asphaltene aggregation. Commercially used alkyl-phenol dispersants are tested with model oils, and the results are visualized. Interestingly, initial asphaltene deposition worsens in the presence of the tested dispersants, but the mechanism by which plugging and permeability reduction in the porous media varies. The deposition tendency is also related to the intermolecular interactions governing the asphaltene-dispersant systems. The combined use of microfluidic devices and rheology offers a unique platform to develop and design effective chemical dispersants for flow assurance problems.

Wednesday 6:30 Woodway II/III

PO7

**Thermal processing of thermogelling nanoemulsions as a route to tune material properties**Li-Chiun Cheng, James Swan, and Patrick S. Doyle*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Soft matter systems have properties which depend on their processing history. It is generally accepted that material properties can be finely tuned by carefully directing self-assembly. However, for gelling colloidal systems, it is difficult to characterize such path-dependent effects since the colloidal attraction is often provided by adding another component to the system. Therefore, studies of and an understanding of the role of

processing on the material properties of attractive colloidal systems are largely lacking. In this work, we systematically studied how processing greatly influences the properties and the microstructures of model attractive colloidal systems. We perform experiments using a thermogelling nanoemulsion as a model system where the isotropic attraction can be precisely tuned via the temperature. The effects of processing conditions on gel formation and properties is tested by performing well-designed sequential temperature jumps. By properly controlling the thermal history, we demonstrate that properties of colloidal gels can be beyond the limit set by direct quenching, which has been a major focus in literature, and that otherwise slow aging of the system associated with a decrease in elasticity can be prevented. Our results provide new experimental evidence of path-dependent rheology and associated microstructures in attractive colloidal systems and provide guidance to future applications in manufacturing complex colloid-based materials

Wednesday 6:30 Woodway II/III

PO8

### **Rheological characterization of mixed surfactant films at droplet interfaces via micropipette aspiration**

Benjamin Micklavzina<sup>1</sup>, Marjorie Longo<sup>2</sup>, and Kostyantyn Lufarov<sup>2</sup>

<sup>1</sup>*Department of Materials Science and Engineering, University of California, Minneapolis, MN, United States;* <sup>2</sup>*Chemical Engineering, University of California - Davis, Davis, CA, United States*

Viscous films comprised of cationic and anionic surfactants can dominate the rheology of micrometer-sized suspended droplets. We studied how films of sodium dodecyl sulfate (SDS) and dodecylamine hydrochloride (DAH) affected the mechanical properties of alkane droplets via a technique known as micropipette aspiration. Using this technique, we were able to measure both the droplet interfacial tension with increasing surfactant concentration and the 2-D film viscosity. We found that a phase transition observed in the bulk alkane emulsion corresponded to a sudden thickening of the film of mixed SDS and DAH. Using fluorescence microscopy, we acquired evidence that the phase change may have corresponded with the appearance of microcrystalline grains at the surface of the droplets. This phenomenon is known to occur for gas bubbles with lipid shells, and our results imply that the presence of such grains could have a strong effect on the apparent mechanics of complex emulsified mixtures of surfactants.

Wednesday 6:30 Woodway II/III

PO9

### **Symmetry-breaking instability of a leaky dielectric drop in a strong electric field**

Jeremy A. Koch and Petia M. Vlahovska

*Engineering Sciences & Applied Mathematics, Northwestern University, Evanston, IL 60202, United States*

In the presence of a uniform electric field, a weakly conducting drop bearing zero net charge will adopt a prolate or oblate spheroidal shape, with both the shape and flow axisymmetrically aligned with the applied field -- a classical result from G.I. Taylor. We describe here a symmetry-breaking instability that develops at higher field strengths. In the case of an oblate drop with a low viscosity relative to the surrounding medium, a secondary flow -- a series of surface vortices -- develops in a belt along the drop equator. This is intriguing, as the system is in the Stokes flow regime, hence the destabilization is not caused by inertia. Further, this vortex belt is not observed at higher drop viscosities. We explore this phenomenon experimentally in a silicone oil/castor oil system, and rationalize the results with a new theoretical model. Beyond the intellectual interest in these three-dimensional nonlinear Stokes flows, these results may be applied to the problem of mixing in viscous fluids, the production of particles with surface patterns, and the design of active materials.

Wednesday 6:30 Woodway II/III

PO10

### **Tuning interaction potentials to modify the structure and rheology of nanoemulsion colloidal gels**

Signe Lin Kuei Vehusheia<sup>1</sup>, Li-Chiun Cheng<sup>2</sup>, and Patrick S. Doyle<sup>2</sup>

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Nanoemulsions are widely used in applications such as food products, cosmetics, pharmaceuticals, and enhanced oil recovery for which the ability to engineer material properties is desirable. Moreover, nanoemulsions are emergent model colloidal systems due to the ease in synthesizing monodisperse samples, flexibility in formulations, and tunable material properties. In this work, we systematically studied a dual-responsive nanoemulsion system developed in our group. The structures and the rheological properties are engineered by manipulating the inter-particle potential through thermally responsive polymer bridging and screening of electrostatic interactions. Our results offer a route to control the material properties of an attractive colloidal system by carefully tuning the interactive potentials and sequentially triggering the colloidal self-assembly. The control and understanding of these properties can be used for designing hierarchically structured hydrogels and complex colloidal-based materials for advanced applications.

Wednesday 6:30 Woodway II/III

PO11

### **Foam formation during drainage of a surfactant solution by gas injection**

Nicolle M. Lima<sup>1</sup>, Shima Parsa<sup>2</sup>, and Marcio S. Carvalho<sup>1</sup>

<sup>1</sup>*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451900, Brazil;* <sup>2</sup>*School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States*

Foam can be used in enhanced oil recovery to maximize oil production and solve problems caused by either a thief zone or gravity override. The presence of liquid lamellae between gas bubbles in the foam reduces the gas mobility; the resistance imposed by drag on moving lamellae resembles a shear-thinning viscosity behavior and leads to a more stable oil displacement flow. The flow mobility is a function of the pore geometry and foam properties. Foams can be injected in the reservoir or produced in-situ in the gas-liquid flow through the pore space. The goal of this

research is to study foam formation during drainage of a two-dimensional porous media glass model by visualizing the pore scale displacement flow of a surfactant solution by injected gas. Image processing is used to study the evolution of the phase distribution and foam characteristics as a function of pore space geometry and flow conditions.

Wednesday 6:30 Woodway II/III

PO12

### **A theoretical model for thermoresponsive nanoemulsions with polymer bridging interactions**

Brian K. Ryu<sup>1</sup>, Tuan Nguyen<sup>2</sup>, Scott Fenton<sup>2</sup>, Matthew E. Helgeson<sup>2</sup>, and Roseanna N. Zia<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Stanford University, Stanford, CA, CA 94305-4125, United States;* <sup>2</sup>*University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

Since antiquity, thermal processing strategies that harness slow dynamics to kinetically arrest phase separations have existed for molecular materials such as metal alloys and ceramics. Through a sophisticated set of quenching, annealing, and tempering strategies, these techniques have led to mesoscopic structures and superior mechanical properties that are otherwise unattainable. For colloidal materials, however, the separation of time scales between colloids and the suspended fluid introduces slow kinetics, thereby complicating the thermal processing of colloidal solids. As a result, thermal processing methods have remained elusive for colloidal systems. The key challenges of studying colloidal materials arise from the difficulty in achieving precise control of interparticle interactions in situ, and in dynamically simulating systems sufficiently large for extended times to observe kinetic and phase behavior while faithfully replicating the physics in silico. In this study, we present results from our large-scale dynamic simulations of a reversible, thermoresponsive bridging nanoemulsion system, in which polymers in the aqueous continuous phase bridge oil droplets via hydrophobic interactions. Helgeson and co-workers have utilized neutron scattering and rheology to establish an interactive potential that accurately describes the model system phase behavior, where the potential parameters that correspond to the depth and range of attraction are modulated in experiment by temperature. In this computational work, we carefully match the polymer bridging interaction to the model for simulation to accurately replicate the kinetics of phase behavior, beginning with the development, testing, and validation of the in silico, temperature-dependent attractive potential.

Wednesday 6:30 Woodway II/III

PO13

### **Considerations of thermal effects in the flow of polymer melts in flat dies during extrusion of cast film**

Olivier Catherine

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Industrial flat film production is very demanding and has experienced extreme manufacturing trends over the last two decades. For example, packaging film produced by cast film process is being made as wider film, thinner gauges, and faster extrusion line speeds. When designing flat film extrusion dies, designers are facing issues related to the strong coupling of the thermal aspects and the fluid mechanics part of the flow. In some cases of high output extrusion, it is challenging to control melt temperature uniformity of the melt stream upstream from the extrusion die. In the presentation we will see some practical results of the thermal aspect of the flow and how it affects extrusion performance. Non-Newtonian, non-isothermal flow simulations are also used to evaluate effects of non-uniform melt temperature flowing into a flat film extrusion die.

Wednesday 6:30 Woodway II/III

PO14

### **Modeling polydisperse polymers in transient and steady extensional flows using the Mead “semi-toy” model**

David W. Mead<sup>1</sup>, Behrouz Behdani<sup>2</sup>, and Joontaek Park<sup>2</sup>

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The new polydisperse Mead-Park “toy” molecular constitutive model [1,2,3] has been quantitatively evaluated with experimental data in fast, transient extensional and shear flows. The bare MP model can only qualitatively simulate arbitrary fast nonlinear flows. The principal reason for this is that since the MP “toy” model completely suppresses the tube coordinate it ignores all contributions to the rheology from contour length fluctuations (CLF). We rectify this serious deficiency by deriving the “semi-toy” Mead model which approximately captures the physics of CLF by only partially suppressing the tube coordinate dependence of the orientation and stretch equations. The new Mead “semi-toy” molecular model quantitatively captures the linear and nonlinear rheology in fast transient shear and extensional flows with a mathematically tractable model that includes entanglement dynamics, contour length fluctuations, configuration dependent friction coefficient (CDFC), reptation, double reptation constraint release, CCR as well as conventional and diluted tube chain stretching. Since CLF's are accounted for, the new Mead “semi-toy” model can simulate polydisperse systems of linear and star polymers in arbitrary slow or fast flows.

Wednesday 6:30 Woodway II/III

PO15

### **Understanding the rheology and dynamics of polymeric mixtures with molecular dynamics**

Oluseye Adeyemi, Kushal Panchal, Ali Heydari Beni, and Li Xi

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Classical theories for polymer dynamics were mostly developed for single-component monodisperse polymer melts, whereas practical applications often involve polymers that are polydisperse, blends, and/or mixtures with additives. Polymer materials produced at industrial scales normally come with a broad molecular weight distribution (MWD) and the effects of the variation in polymer chain lengths on the melt rheology is less understood. On the other hand, quantitative knowledge of this relationship can also enable new methods for determining the MWD from rheological measurements. In another example, many polymer materials are manufactured with plasticizers but the fundamental knowledge



regarding what kinds of molecular features and interactions are responsible for plasticization effects, including the reductions in the glass transition temperature  $T_g$  and tensile and shear moduli, is limited. Ongoing projects in our group using molecular dynamics for the fundamental understanding of polymer mixture rheology will be discussed. Equilibrium and non-equilibrium approaches are being used to study the effects of chain length distribution on linear viscoelasticity. Signal processing techniques are explored for the noise reduction in stress time series from molecular simulation for reliable prediction. The effectiveness of different approaches will be compared. For the particular mixture between a long-chain polymer and small-molecule additives, the effects of additive size, interaction with the host polymer, and molecular design on the plasticization effectiveness will be discussed. In particular,  $T_g$  of the mixture is found to display a complex dependence on additive size, indicating that a simple free volume or dilution argument is not sufficient to explain the plasticization effect.

Wednesday 6:30 Woodway II/III

PO16

### **Strain shifts in stress-controlled oscillatory shear: Probing zero-shear viscosity and TTS shifting factors of polymer melts**

Ching-Wei Lee and Simon A. Rogers

*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Strain responses under stress-controlled oscillatory shearing often oscillate about a non-zero value. Conventionally, the strains are shifted so that they oscillate about zero, and the corresponding shifting factors are ignored. Investigating three distinct types of polymer systems, including polymer-like micelles, concentrated polyethylene oxide solutions, and molten entangled polystyrene, we show that the shifted strain is a manifestation of a moving equilibrium strain, and a theory describing the shifting is provided. We further demonstrate that the shifting factors collected at different imposed frequencies and stress phases can be superimposed into one master curve. These strain shifting factors contain information about fundamental material properties, and are shown to be an alternative measure of zero-shear viscosity. The zero-shear viscosity can be independently and efficiently measured in the linear regime across distinct regimes of dynamics, including the terminal and Rouse regimes, and the rubbery plateau, where avoiding edge fracture is crucial. This approach can be further applied to *directly* determine the time-temperature superposition (TTS) shifting factors. In-situ time-resolved small-angle neutron scattering under varying stress imposes confirms that microstructural evolution is independent of the shifted lab-frame strain, yet correlates well with the recoverable strain.

Wednesday 6:30 Woodway II/III

PO17

### **Configurational microphase separation in elongational flow of an entangled polymer liquid**

Mohammad Hadi Nafar Sefiddashti, Brian J. Edwards, and Bamin Khomami

*Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, United States*

Net-shape manufacturing of plastic and rubber products is typically performed via processing of a molten polymeric fluid under an imposed flow field. Until recently, the general state of knowledge has maintained that the orientation and deformation of the constituent chain-like molecules under flow is homogeneous and essentially obeys Gaussian statistics; however, recent experimentation and simulation have called this notion into question.

NEMD simulations for the planar elongational flow of a  $C_{1000}H_{2002}$  polyethylene liquid revealed a new, unexpected phenomenon; *i.e.*, a bimodal distribution of molecular extension was observed at intermediate flow strengths in the range of  $0.3 \leq De \leq 1.5$ . These two peaks correspond to a tightly coiled configurational state and a highly stretched state at intermediate  $De$ , thus providing clear evidence of a system with a bistable steady state. The visualization of the system in this flow strength range revealed that the bistable configurational states not only coexist, but also that the constituent molecules become segregated via an inhomogeneous microphase separation into large domains of relatively coiled molecules that are surrounded by thinner regions of highly stretched chains. Such startling behavior represents a remarkable departure from the theoretical expectation, and as such, it is not an intuitive process to assimilate.

Wednesday 6:30 Woodway II/III

PO18

### **Characterizing the impact of shear and cooling conditions on crystallinity of a polymer melt**

James P. Eickhoff

*Anton Paar USA, Ashland, VA 23005, United States*

Understanding morphology is critical in polymer rheology as the degree of crystallization can greatly impact various material properties. The solidification of a semi crystalline polymer is more impacted by the increase in crystallinity than by the decrease in temperature. This change in crystallinity can influence the flowability of the polymer during processing. Understanding how to characterize as well as control this behavior is vastly important from a processing standpoint. In this work, isotactic polypropylene was measured under quiescent conditions with varying cooling conditions to investigate the onset of crystalline growth in the polymer melt. Additional measurements were carried out to study the influence of shear on the crystalline growth during cooling. Visualization of these measurements were performed with an optical module that has been adapted to a rotational rheometer for studies at processing conditions. This combination allows for the visco-elastic properties of a material to be characterized while changes in the morphology can be studied through microscopic imaging, in the form of either pictures or videos.

Wednesday 6:30 Woodway II/III

PO19

**In-situ Rheo-SAXS study on shear alignment of ABA triblock copolymers with closed packed spherical morphology**Wenyue Ding<sup>1</sup>, Wesley Burghardt<sup>2</sup>, and Megan Robertson<sup>1</sup><sup>1</sup>*Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX, United States;* <sup>2</sup>*Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, United States*

Block copolymer morphologies formed spontaneously from the melt state lack long range order. Application of external forces, such as shear, electric fields, or magnetic fields, can lead to alignment of microdomains. In this study, a microphase-separated poly(styrene-*b*-(lauryl-co-stearyl acrylate)-*b*-styrene) triblock copolymer, exhibiting a disordered spherical microdomain with randomly oriented spheres, was aligned through the application of oscillatory shear in the nonlinear region. Strain sweep measurement revealed three shear regions: small amplitude oscillatory shear (SAOS), median amplitude oscillatory shear (MAOS) and large amplitude oscillatory shear (LAOS). Shear alignment experiments were performed in both MAOS and LAOS regions. Highly aligned close packed spherical morphology was observed after application of oscillatory shear, independent of the strain amplitude. The alignment kinetic has been investigated in detail through Rheo-SAXS. Degree of alignment was monitored throughout the course of shearing, and fitted with stretched exponential function. With same frequency, higher strain exhibited lower characteristic ordering time, indicating faster ordering kinetic. A better macroscopic orientation was achieved in LAOS region. Interestingly, the degree of alignment at highest shear amplitude ( $\gamma=150\%$ ) exhibited a maximum at short time, then unexpectedly decreases with longer shearing time.

Wednesday 6:30 Woodway II/III

PO20

**Long-lived neighbours determine the rheological response of glasses**Marco Laurati<sup>1</sup>, Philipp Maßhoff<sup>2</sup>, Kevin J. Mutch<sup>2</sup>, Stefan U. Egelhaaf<sup>2</sup>, and Alessio Zaccone<sup>3</sup><sup>1</sup>*Universidad de Guanajuato, Leon, Mexico;* <sup>2</sup>*Heinrich-Heine University Düsseldorf, Düsseldorf, Germany;* <sup>3</sup>*University of Cambridge, Cambridge, United Kingdom*

Using an advanced combination of rheology and confocal microscopy, we investigate the transition to flow of colloidal glasses. In particular, structural and dynamical information is collected and combined to relate the yielding transition to the rearrangement and breaking of the cage of neighbors. This is quantified by the mean squared nonaffine displacement and the number of particles that remain nearest neighbors for a long time, i.e., long-lived neighbors, respectively. Both quantities are followed under shear using confocal microscopy and are the basis to calculate the affine and nonaffine contributions to the elastic stress, which is complemented by the viscoelastic stress to give the total stress. During start-up of shear, the model predicts three transient regimes that result from the interplay of affine, nonaffine, and viscoelastic contributions. Our prediction quantitatively agrees with rheological data and their dependencies on volume fraction and shear rate [1].

[1] M. Laurati, P. Maßhoff, K. J. Mutch, S. U. Egelhaaf, and A. Zaccone, *Phys. Rev. Lett.*, 118, 018002 (2017)

Wednesday 6:30 Woodway II/III

PO21

**Thermodynamic description of shear-induced phase transition in jammed soft particle glasses**Fardin Khabaz<sup>1</sup>, Michel Cloitre<sup>2</sup>, and Roger T. Bonnecaze<sup>1</sup><sup>1</sup>*University of Texas at Austin, Austin, TX, United States;* <sup>2</sup>*ESPCI ParisTech, Paris, France*

Recently we computationally showed that jammed suspensions of soft particles can undergo a phase transition under steady (Khabaz et al. *Phys. Rev. Fluids.* 2, 093301 (2017)) and oscillatory (Khabaz et al. *Phys. Rev. Fluids.* 3, 033301 (2018)) shear flows and form variety of ordered microstructures. In particular using the three-dimensional particle-dynamics simulation, we demonstrated that polydisperse suspensions formed a layered microstructure parallel to the flow-vorticity plane at high shear rates. The formation of the layered microstructure significantly decreases the internal energy and entropy of the system. Although the thermal forces are negligible in our model for jammed suspensions of soft particles due to the significance of the elastic forces between particles at contact, we can define an effective temperature using the excess entropy and elastic energy of the system. Rosenfeld theory, which connects the excess entropy to the microstructure of a system, is employed to quantify the excess entropy of the glassy and layered suspensions under different shear rates and volume fractions. Our results at a given shear rate show that the temperature and Helmholtz free energy of the layered microstructure is lower than that of the glassy suspensions. Both temperature and Helmholtz free energy follow a similar trend as the flow curve of these materials, i.e. an increase in the shear rate in each state increases the temperature and elastic energy of the suspension. In addition, the defined temperature exhibits an approximately linear relationship with the shear stress and elastic energy, which indicates that in a jammed state of these soft suspensions the shear stress can play the temperature role.

Wednesday 6:30 Woodway II/III

PO22

**A model for the depletion layer prediction in a dilute suspension of rigid rod-like particles under shear flows in the entire range of Peclet numbers**

Saman Monjezi and Joontaek Park

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We derived a semi-analytical model to predict the concentration profile, or the center-of-mass distribution, of rod-like particles near a wall under shear flows. Different excluded volume mechanisms of a rod near a wall in each Peclet number (a ratio of shear rate and diffusivity) regime were incorporated into the model through a steric factor concept. At low and moderate Peclet numbers, the steric factor is mainly determined by the

ratio of the restricted/unrestricted rod orientation distributions. However, at high Peclet number number, the ratio between the rod penetration time in a depletion layer and the Jeffery orbit frequency mainly affects the steric factor. The predicted concentration profiles showed a good agreement with the results from previous works.

Wednesday 6:30 Woodway II/III

PO23

### **Prediction of residual stresses in soft glassy materials using a multi-mode structural kinetic model**

Raghav Kumar and Yogesh M. Joshi

*Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India*

Soft glassy materials are highly viscous soft materials that are thermodynamically out of equilibrium, which undergo structural evolution as a function of time. The process of structural evolution causes decrease in free energy, a process known as physical aging. The application of deformation field on the other hand causes structural breakdown that, in principle, increases free energy, a process known as rejuvenation. Many soft glassy materials, under application of constant strain subsequent to shear melting, often demonstrate residual stresses that do not decay over the practical timescales. Interestingly with increase in intensity of shear melting some materials show increase in the magnitude of residual stresses while other materials show decrease in magnitude of residual stresses. In this work, we employ a multi-mode structural kinetic model that employs Sprigg's relaxation time spectra. We observe that the diverse experimental observations can be captured by varying the width of relaxation time spectrum.

Wednesday 6:30 Woodway II/III

PO24

### **Shear flow affects the morphology and the growth kinetics of salt aggregates**

Luca Sicignano, Giovanna Tomaiuolo, Antonio Perazzo, and Stefano Guido

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Colloids flowing through micro-sized channels might be deposited onto the wall surfaces through diffusion-controlled mechanisms. In the last decade, continuous flow operation has become an increasingly popular route for chemical synthesis, exhibiting a large number of advantages with respect to traditional batch reactors, also due to the development of microreactors<sup>1,2</sup>. However, flow confinement in microfluidic-based systems can also give rise to some drawbacks, such as solid precipitation and aggregation, eventually leading to microchannel clogging and thus making solid handling a key issue in microreactors<sup>3,4</sup>. Here, it is described how a continuous-flow pharmaceutically relevant synthesis for the production of arylamines can be harnessed to avoid or manipulate the production of salt crystals within glass microchannels. It is found that shear flow in the laminar regime affects both morphology and growth of salt aggregates and that cluster formation starts at the wall, likely due to the velocity profile, which promotes particle/wall interactions. We discuss the effect of flow strength and channel glass walls on the nature of the salt crystals highlighting the role of simplified chemical mechanisms<sup>5</sup>. Our findings provide information about the surface deposition of a crystal that are useful for an improved understanding of crystal growth in porous media and for a better control of a pharmaceutically relevant synthesis.

<sup>1</sup> M. J. Jebrail et al, Lab on a Chip, 2012, 12, 2452-2463. <sup>2</sup> A. Pommella, G. Tomaiuolo, et al., Chemical engineering journal, 2013, 223, 578-583.

<sup>3</sup> S. Falß, G. Tomaiuolo, et al., Organic Process Research & Development, 2016, 20, 558-567. <sup>4</sup> A. Perazzo, G. Tomaiuolo, et al., RSC Advances, 2015, 5, 63786-63792. <sup>5</sup> L. Sicignano, G. Tomaiuolo, et al., Chemical Engineering Journal, 2018, 341, 639-647.

Wednesday 6:30 Woodway II/III

PO25

### **The hydrodynamics of the colloidal glass transition via parallelized accelerated Stokesian dynamics**

Monica E. A. Zakhari, Gaddiel Ouaknin, Jialun Wang, and Roseanna N. Zia

*Chemical Engineering, Stanford University, Stanford, CA, CA 94305-4125, United States*

The colloidal glass transition has been a challenging task for researchers for the past few decades, owing primarily to the divergence of the timescales near the jamming transition. Furthermore, colloidal systems exhibit aging; the system continuously relaxes over time at high densities and complete arrest may not be reached. In this work, we aim at identifying the microscopic mechanism for the glassy arrest and its connection with the aging phenomenon manifested by these systems. This poster presents a detailed study of the colloidal glass transition using large-scale Stokesian dynamics simulations. We perform well-controlled volume fraction jumps from an equilibrated liquid state to the glassy state with different quench depths up to random-close packing and aging times. In addition, the evolution of the mechanical and structural properties is used to unravel the effect of many-body hydrodynamic forces and lubrication on the glass transition which have been poorly understood.

Wednesday 6:30 Woodway II/III

PO26

### **The rheology of a spherically confined Brownian suspensions**

Alp M. Sunol and Roseanna N. Zia

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Modeling the motion of colloids in spherically confined environments is crucial to understanding the motion of particles inside living cells, bio-reactor droplets, inkjet printing, and more. A key aspect of such motion is the interplay between crowding (particle concentration) and confinement (the size of the enclosing cavity relative to the suspended particles). Here we present the results of our dynamic simulations studies of the osmotic pressure, diffusion, and structure both at equilibrium and away from equilibrium, the latter as a model for intradroplet stirring by heavier (sedimenting) particles, using our Confined Brownian Dynamics computational algorithm. We find an interesting interplay between 'internal crowding' (particle volume fraction), confinement-induced crowding, and osmotic pressure that has a satisfying connection to the volume-fraction

dependent, anisotropic, spatially heterogeneous diffusion tensor. The sedimentation velocity provides measurement of a spatially heterogeneous, Pe-dependent microviscosity, which we then connect to osmotic pressure and diffusion.

Wednesday 6:30 Woodway II/III

PO27

### **Effect of pH conditions on rheological characteristics of boehmite suspensions**

Gi Wook Lee, Da Young Lee, Byoungjin Chun, and Hyun Wook Jung

*Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea*

Aluminum oxide, e.g., boehmite, is one of the typical ceramic catalyst supports used in various fields such as exhaust gas filters, enhancing the durability and catalyst activity as the carrier for precious metal catalysts. To uniformly coat catalytic suspensions or slurries on a filter substrate, their macro-/micro-rheological features should be well characterized. Rheological properties of boehmite suspensions, such as viscoelasticity and particle dynamics, are importantly affected by the internal structure and dispersion stability of particles dispersed in a continuous medium. In suspensions, Van der Waals force and electrostatic force between particles are closely related to the surface charge of particles and their structures. In this study, catalytic suspensions with rod-like boehmite particles are produced at different pH levels. The effect of applied pH condition for boehmite suspensions on the macro-rheological properties (e.g., shear viscosity, elastic/viscous moduli, and rheological change in oscillation-rotation-oscillation mode) is scrutinized using a rheometer. Also, the apparent particle size distribution and the temporal motions of particles were identified by using dynamic light scattering (DLS) and multi-speckle diffusing wave spectroscopy (MSDWS).

Wednesday 6:30 Woodway II/III

PO28

### **Tracer transport probes relaxation and structure of attractive and repulsive glassy liquids**

Ryan C. Roberts, Ryan Poling-Skutvik, Jeremy C. Palmer, and Jacinta C. Conrad

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Dynamic coupling of small penetrants to slow, cooperative relaxations within crowded cells, supercooled liquids, and polymer matrices has broad consequences for applications ranging from drug delivery to nanocomposite processing. Similarly, understanding the dynamics of dopants is crucial for interpreting experiments that probe viscosity during vitrification. Interactions between the constituents of these and other disordered media alter the cooperative relaxations, but their effect on penetrant dynamics remains incompletely understood. We use molecular dynamics simulations to show that the motions of hard-sphere tracer particles probe differences in local structure and cooperative relaxation processes in attractive and repulsive glassy liquid matrices with equal bulk packing fractions and long-time diffusivities. Coupling of the tracer dynamics to collective relaxations in each matrix affects the shape of tracer trajectories, which are fractal within the repulsive matrix and more compact in the attractive. These results reveal that the structure of relaxations controls penetrant transport and dispersion in cooperatively relaxing systems and provide insight into dynamical heterogeneity within glassy liquids.

Wednesday 6:30 Woodway II/III

PO29

### **Image cytometry of irregular microplastic particles in cross-slot microchannel utilizing viscoelastic focusing**

Bookun Kim<sup>1</sup>, Hwang Lee<sup>2</sup>, Seong Jae Lee<sup>3</sup>, Jung Hwan Kwon<sup>4</sup>, and Ju Min Kim<sup>1</sup>

<sup>1</sup>*Department of Energy Systems Research, Ajou University, Suwon, Republic of Korea;* <sup>2</sup>*Division of Environmental Science and Ecological Engineerin, Korea University, Seoul, Republic of Korea;* <sup>3</sup>*Department of Polymer Engineering, The University of Suwon, Hwaseong Gyeonggi-do, Republic of Korea;* <sup>4</sup>*Division of Environmental Science and Ecological Engineerin, Korea University, Seoul, Republic of Korea*

Microparticles are used in a variety of fields such as cosmetics, food industry, coatings, and drug delivery. Nonuniform particle distribution that occurs during the drying process, called “coffee ring effect”, can be significantly suppressed by using ellipsoidal particles [1]. So, it is very important to accurately measure the size of these particles because the size distribution of the particles greatly affects molding, drying and calcination. Various methods such as scanning electron microscope (SEM) or observation under optical microscopes have been used to measure the particle size. However, unlike spherical particles, non-spherical particles are difficult to accurately measure the shapes because of the tilting of the particles and out of optical view focusing. In this work, we demonstrate that the cross-clot microchannel can be used artificial planar extensional flow for the shape measurement of oblate-shaped microparticles in a similar way to the previous work.[2] In addition, irregular debris microparticles were morphologically analyzed.

References [1] Yunker et al., *Nature*, 476, 308-311 (2011). [2] Kim et al., *Anal. Chem.*, 89, 8662-8666 (2017).

Wednesday 6:30 Woodway II/III

PO30

### **Concentrated suspensions of noncolloidal conductive particles in an electric field: Suspension dynamics and rheology**

Jae Sung Park and Siamak Mirfendereski

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The suspension dynamics and rheological behavior of concentrated non-Brownian suspensions undergoing nonlinear electrokinetics have been studied using Stokesian dynamics simulations. The ideally polarizable sphere suspensions at various particle volume fractions up to the packing fraction are investigated. The uniform electric field is applied in the vertical direction relative to the suspension volume. The velocity fluctuation of the suspension shows nontrivial behavior as the suspension volume fraction increases. Initially, the velocity fluctuation increases with the

volume fraction, while it starts to decrease at a semi-dilute regime. However, it returns to increasing at a higher volume fraction, and then suddenly decreases when approaching the packing fraction. This nontrivial behavior is explored by calculating the pair distribution function for the local microstructure of the suspensions. It is shown that the pair distribution of concentrated suspensions is characterized by the sharp peak at the equator of the particles, as opposed to the dilute and semi-dilute suspensions where the peak is located at the pole. In addition, the peak region appears to be almost uniform over the particle surface at the packing fraction. Lastly, the rheological properties are calculated, and the relationship between suspension rheology and the system microstructure is further discussed.

Wednesday 6:30 Woodway II/III

PO31

### **Probing the effects of shear energy and interfacial chemistry on the yield stress and aggregate structure of model thickened tailings**

Ravi Neelakantan<sup>1</sup>, Farid Vaezi<sup>2</sup>, and R S. Sanders<sup>3</sup>

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The disposal of mineral tailings is a complex endeavor, due in no small part to the non-Newtonian, time-dependent and shear-dependent rheology exhibited by such mixtures. Mineral tailings can be treated with different polymers to concentrate the suspension, thereby reducing tailings volumes and recovering water for recycle. The resulting tailings mixture is a high-density fluid with a complex and time-dependent rheology. When subjected to shear, the thickened tailings undergoes a permanent reduction in yield stress due to break-down and restructuring of aggregates, further exacerbating the complexity of the problem. While the effect of shear on aggregates in dilute suspensions has been studied, its impact on rheology in more concentrated, polymer-amended suspensions is not well understood. In the present study, we use a custom-built concentric cylinder shearing apparatus to apply known amounts of shearing energy to a large volume of model (kaolinite) thickened suspensions. Using the custom apparatus, particle size distributions (PSD) and rheology were monitored as a function of shear energy input using the Focused Beam Reflectance Measurement (FBRM) and vane yield stress techniques, respectively. Concentrated suspensions were prepared using four different flocculants, and at two different pH values to evaluate the effect of varying interfacial interactions between clays and polymers on aggregate size and mixture yield stress evolution under shear. Changes in aggregate structure and yield stress correlated directly with shearing energy. The suspension behavior varied substantially depending on the pH and polymer structure. After some amount of shearing, a large population of smaller aggregates in the range of 10-100 $\mu$ m is generated, which eventually occupy the largest volume fraction of solids. The inter-particle associations within the small aggregates, which are affected by both pH and polymer type, dictate the equilibrium (fully-sheared) yield stress of the suspensions.

Wednesday 6:30 Woodway II/III

PO32

### **Effect of flow types on agglomerate breakup in a Newtonian fluid**

Seung Hui Kim, Jaehwan Jeong, and Kyung Hyun Ahn

Seoul National University, Seoul, Republic of Korea

Heterogeneity control of colloidal dispersion is deeply related with productivity. The particles dispersed in a fluid can easily form agglomerates, which can also be separated into small aggregates of various size and morphology upon the flow field. In this work, we investigate the change of microstructures of the agglomerates under four viscometric standard flows, which are simple shear, uniaxial, biaxial and planar elongational flow. Brownian dynamics simulation is used to describe particle dynamics and DLVO potential is used as an interparticle potential. Fractal dimension and the size of the agglomerates are used to classify the agglomerates. Three structural analysis methods are used to quantitatively analyze the change of morphologies under four flow fields, which are fragment size distribution, bond number distribution and largest cluster size. Fragment size distribution gives us the relationship between the number of fragments and fragment size with respect to the flow type. Bond number distribution can explain which flow is most efficient for breakup which is directly connected to solution heterogeneity. Tracking largest cluster size over time gives an idea on the reconstruction, erosion and rupture as well as the difference between shear and elongational flow.

Wednesday 6:30 Woodway II/III

PO33

### **Three region rheological and order parameter behavior in nanocylinder dispersions**

Matthew M. Noor<sup>1</sup>, Katie M. Weigandt<sup>2</sup>, Martin J. Pospisil<sup>3</sup>, Micah J. Green<sup>3</sup>, and Virginia A. Davis<sup>1</sup>

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There is significant interest in producing macroscale materials with anisotropic optical, mechanical, or electrical properties via the controlled fluid phase assembly of rod-like nanomaterials. However, there is still relatively limited understanding of these systems' phase behavior, rheological properties and microstructural relaxation after shear cessation. In this study, rheology and rheo-optics were used to understand the behavior of two aqueous lyotropic systems: sulfonated cellulose nanocrystals (CNC) and double-stranded DNA stabilized single-walled carbon nanotubes (dsDNA/SWNT). In addition, a combination of rheology and small-angle neutron scattering (RheoSANS) were used to measure changes in the viscosity and flow-oriented order parameter as a function of shear rate for lyotropic dispersions of nanocylinders dispersed in deuterium oxide (D<sub>2</sub>O). In contrast to plots of viscosity versus shear rate, the order parameter trends show three distinct rheological regions over a range of concentrations. This finding is significant because the existence of three rheological regions as a function of shear rate is a long-standing signature of liquid crystalline phases composed of rod-like polymers. However, observing this trend has been elusive for high-concentration dispersions of anisotropic nanomaterials. The results of this work are valuable for guiding the development of processing methodologies for producing ordered materials from nanocylinder dispersions.

Wednesday 6:30 Woodway II/III

PO34

**Experimental and computational studies of the sedimentation of non-orientable objects**Nicolas Moreno, David Vazquez-Cortes, and Eliot Fried*Okinawa Institute of Science and Technology, Onna, Japan*

We study experimentally and computationally the sedimentation of rigid non-orientable shapes, also known as Möbius bands. We explore the effect of the geometrical features of these objects on their motion and the surrounding fluid. For the experimental prototype, we investigate the sedimentation of 3D-printed polystyrene bands in water and water-glycerol mixtures. Additionally, we use a particle-based discretization of the bands and the fluid to construct the computational models. For both, experimental and computational models we evaluate bands with different aspect ratios and orientation of the twist. We also compare the behavior of the Möbius bands with their counterpart hollow cylinders (non-twisted band). We find that due to the geometrical features of these objects rotational and translational motions are coupled, giving rise to a complex sedimentation behavior describing helicoidal paths. In the case of non-twisted bands, the rotational motion is absent due to symmetry constraints. We show that the dimensions of the bands allow us to control the frequency of their dominant motions and to prescribe the amplitude of the path. The hydrodynamic properties of these objects offer an interesting number of applications, including chiral-tracing, mixing, and separation in medical or microfluidics applications, and as prototypes for passive swimmers.

Wednesday 6:30 Woodway II/III

PO35

**Untying of complex knots on stretched polymers in elongational fields**Beatrice W. Soh, Alexander R. Klotz, and Patrick S. Doyle*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States*

Knotting is a prevalent phenomenon which occurs in long polymer chains. We perform Brownian dynamics simulations and single-molecule DNA experiments to investigate knot untying in elongational fields that is induced by the knot being convected off the chain. The change in knot size as the knot moves off the chain and unties causes a change in the effective Weissenberg number, which in turn leads to a change in chain extension. Large scale chain conformational changes are observed in both simulations and experiments for complex knots at low  $Wi$ . We investigate the knot untying time and untying-induced change in extension for a range of knot types and field strengths. The change in extension due to knot untying is found to scale quadratically with initial knot size for  $Wi > 1.5$ . Due to the changes in chain extension as a knot unties, the untying process can be diffusion- or convection-driven.

Wednesday 6:30 Woodway II/III

PO36

**Direct visualization of comb polymer dynamics in semi-dilute solutions using single molecule studies**Shivani F. Patel and Charles M. Schroeder*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Branched polymers play a key role in modern technology and advanced materials. Despite their increasing importance, our current understanding of the non-equilibrium dynamic behavior of these topologically complex polymers is limited and is largely based on bulk rheological and experimental scattering data. Owing to their complex molecular architectures, comb-shaped polymers exhibit rich dynamic behavior that is not fully understood at the molecular level. To address this, we study the dynamics of single branched polymers in non-dilute solutions using single-molecule fluorescence microscopy (SMFM). In particular, we use a hybrid enzymatic-synthetic approach to synthesize DNA-based branched polymers (comb polymers) that contain a long backbone with multiple side branches grafted at various positions. Following synthesis, we directly study the relaxation dynamics of single comb polymers in non-dilute solutions of linear unlabeled polymers in extensional flow and compare them to the dynamics of comb polymers in ultra-dilute solutions. These studies are extended to transient stretching and steady-state stretching dynamics, as well. Interestingly, the dynamic behavior of comb polymers is markedly different in non-dilute polymer solutions, which reveals changes in molecular-scale dynamics due to chain branching and chain-chain intermolecular interactions. We further study the effects of background concentration and polymer topology on comb polymer dynamics in order to elucidate the non-equilibrium behavior of topologically complex polymers. Overall, our work shows that single polymer dynamics can be used to provide a direct link between polymer microstructure and bulk rheological properties.

Wednesday 6:30 Woodway II/III

PO37

**A study of the linear and nonlinear viscoelastic properties of cyclic poly(3,6-dioxa-1,8-octanedithiol) (polyDODT)**Dongjie Chen<sup>1</sup>, Gregory B. McKenna<sup>1</sup>, Judit E. Puskas<sup>2</sup>, Carin A. Helfer<sup>2</sup>, Zhiyuan Qian<sup>1</sup>, and Julia A. Kornfield<sup>3</sup>*<sup>1</sup>Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; <sup>2</sup>Departments of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH 44325-0406, United States; <sup>3</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States*

Rheology of ring-like or circular polymers remains an area of active research due to the difficulty of making ring polymers of sufficient purity free of linear contaminants. Furthermore, past work has been limited to rings made in dilute solution and, consequently, have been limited to sizes of approximately 15 entanglements in the linear analog. Furthermore, synthesis in dilute solution results in small amounts of material being available for study. This problem has been overcome by reversible radical recombination polymerization (R3P) recently developed in the Puskas

laboratories. R3P synthesis can produce 10-100g scale circular polymer which opens new avenues of research. Here we have studied poly(3,6-dioxa-1,8-octanedithiol) (polyDODT) synthesized by R3P of different molecular weights and solutions of polyDODT solution as a function of concentration using linear dynamic measurements and single and double step strain experiments to explore the nonlinear rheology. Of interest is that the largest polyDODT ring investigated to date has a molecular mass corresponding to approximately 100 entanglements in the linear counterpart. By characterizing the properties as a function of molecular weight and solution concentration it is expected that new information concerning ring dynamics and ring/linear mixture dynamics will be achieved. Preliminary results from our studies will be presented.

Wednesday 6:30 Woodway II/III

PO38

### **Dynamics of filamentous viral nanoparticles in semi-dilute polymer solutions**

Maxwell Smith, Ryan Poling-Skutvik, Richard C. Willson, and Jacinta C. Conrad

*Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States*

Bacteriophage, viral nanoparticles that infect bacteria, are widely used as uniform, anisotropic building blocks for applications in electronics and sensing. These applications often require bacteriophage (phage) to be controllably transported through complex fluids that contain polymers, macromolecules, or proteins. As one example, phage employed as reporter particles in ultrasensitive lateral-flow assays must be transported through biological fluids to capture sites on a functionalized membrane - with the assay sensitivity depending in part on the efficient transport of phage. How nanoparticle anisotropy affects transport in complex fluids in which characteristic length scales of the fluid and particles are comparable, however, remains incompletely understood. Here, we investigate the dynamics of phage with varying aspect ratios in semi-dilute polymer solutions using fluorescence microscopy. Phage diffuse faster than predicted by the Stokes-Einstein relation using the bulk viscosity of the polymer solutions. The normalized diffusivity of the phage is approximately constant at low polymer concentration and then decreases at a crossover polymer concentration. Normalized length scales based on the ratio of phage scales (radius, length) to the polymer correlation length were unable to collapse the diffusivities onto those of spherical particles. This result suggests that an intermediate length scale, between phage length and radius, controls phage diffusion through a crowded medium. These results provide insight into the transport behavior of anisotropic phage and, more broadly, are expected to guide the development of applications that exploit particle anisotropy to generate unique functional properties in composite materials

Wednesday 6:30 Woodway II/III

PO39

### **Rheology of ultra-high molecular weight ring polymer solutions**

Sourya Banik and Gregory B. McKenna

*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Rheology of ring polymers have piqued the interest of researchers to study the effect of absence of chain ends on entanglement. In the current endeavor, we study the rheological properties of monodisperse solutions of double stranded covalently closed circular (ccc) DNA molecule extracted from the genome of *Staphylococcus epidermidis* (molecular weight-  $2.4 \times 10^6$  base pairs or  $1.6 \times 10^9$  g/mol). Solutions of such ultra-high molecular weight rings can achieve more than 600 entanglements/ chain for a concentration of 1 mg/ml. The rheological response of the closed ring DNA molecules in the entangled regime is being studied and compared with their corresponding linear counterparts. Effect of concentration and mixtures of rings and linear blends are also being studied to investigate each of its effects on the measured rheological properties.

Wednesday 6:30 Woodway II/III

PO40

### **Study on the vortex dynamics of DNA solution in expansion-contraction array microchannel**

Sun Ok Hong and Ju Min Kim

*Department of Energy Systemes Research, Ajou University, Suwon, Republic of Korea*

Viscoelastic flow passing through a contraction/expansion geometry is relevant in a wide range of applications such as polymer processing, and it has been investigated in microfluidic channels to study the detailed fluid dynamics under various inertio-elastic condition. Vortex dynamics in a contraction/expansion geometry is affected by the geometric conditions such as the aspect ratio in contraction-expansion region as well as the rheological properties of the polymer solution. However, the previous works mainly focus on the viscoelastic flow dynamics in a single contraction/expansion geometry. In this study, we designed the expansion-contraction array microchannel to study the evolution of the vortex dynamics in dilute DNA solutions. The PDMS-based microfluidic device is composed of an array of 25 well pairs attached on both side of a straight channel which has a 50  $\mu\text{m}$  square cross-section and the aspect ratio of the expansion-straight region is 9. We observed the transition of the vortex dynamics from lip to corner vortex with increasing elasticity, which is attributed to the gradually increased stretching of DNA molecules, while DNA molecules are moving from an inlet to downstream. Further, we report that the vortex dynamics in the expansion-contraction array may be affected by the break-up of DNA molecules.

Wednesday 6:30 Woodway II/III

PO41

### **High-pressure linear viscoelasticity measurements of polymer solutions and gels**

Kimberly A. Dennis<sup>1</sup>, Yan Gao<sup>2</sup>, Alhad Phatak<sup>2</sup>, and Eric M. Furst<sup>1</sup>

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Enhanced oil recovery (EOR) fluids are polymer solutions and gels that are designed to transport and suspend solids, reduce friction, and prevent fluid loss. EOR fluid performance depends on its viscosity and elastic modulus. To address the need to characterize the viscoelasticity of EOR fluids under operating conditions, we developed a passive microrheology experiment capable of generating pressures up to 200 MPa. The apparatus

incorporates a sealed steel alloy sample chamber with dual sapphire windows into a diffusing-wave spectroscopy (light-scattering) experiment. The measured light intensity correlation arising from the Brownian motion of polystyrene probe particles dispersed in the sample is interpreted using the Generalized Stokes-Einstein Relation (GSER) to determine the material creep compliance. We validate this high-pressure microrheology instrument by measuring the increase in viscosity of 1-propanol aqueous solutions and extend the measurement to EOR fluids containing poly(vinyl) alcohol polymer and borate as a physical crosslinker. Sample loading methods were designed to prevent the introduction of bubbles, which inhibits pressurization by increasing the sample compressibility. However, these methods were limited to low modulus samples that could be easily loaded with a syringe and needle. New methods for increasing the operating regime to nonergodic gel samples as well as higher temperatures have been developed. We investigate the effect of pressure on the crosslink density and rheological properties at frequencies up to 1 MHz and pressures to 200 MPa.

Wednesday 6:30 Woodway II/III

PO42

### **Simulating nanoparticle dynamics in semidilute polymer solutions with multiparticle collision dynamics**

Renjie Chen<sup>1</sup>, Ryan Poling-Skutvik<sup>1</sup>, Arash Nikoubashman<sup>2</sup>, Michael P. Howard<sup>3</sup>, Sergei A. Egorov<sup>4</sup>, Jacinta C. Conrad<sup>1</sup>, and Jeremy C. Palmer<sup>1</sup>

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The dynamics of nanoparticles in complex fluids are of great interest for applications in drug delivery, oil recovery and materials processing. Particle mobility is well described by the generalized Stokes-Einstein (GSE) relation when the nanoparticles are much larger than the polymers. Violations of GSE predictions are observed, however, when the size of nanoparticles is comparable to or smaller than length scales in polymer solutions.<sup>1</sup> We investigate the microscopic origin of this anomalous behavior using advanced particle-based simulation techniques,<sup>2</sup> with the multiparticle collision dynamics<sup>3</sup> (MPCD) scheme providing a computationally efficient route to modeling solvent-mediated hydrodynamic interactions in nanoparticle-polymer systems. We demonstrate that the translational center-of-mass motions of both nanoparticles and polymers are subdiffusive on short times before transitioning into a diffusive regime on longer time scales.<sup>2</sup> The long-time diffusivities of nanoparticles collapse according to scaling predictions.<sup>4</sup> The sub-diffusive exponents of nanoparticles and polymer centers-of-mass are highly correlated, suggesting that polymer center-of-mass translational motions as well as local polymer relaxations play a role in the coupling between the dynamics of polymers and nanoparticles. Finally, we perform simulations in which we tune the flexibility of the polymers. As the persistence length of the polymers increases, the nanoparticle dynamics become more subdiffusive and decouple from the dynamics of the polymer chain center-of-mass.

References: [1] R. Poling-Skutvik, R. Krishnamoorti, and J. C. Conrad, ACS Macro Lett., 2015, 4, 1169-1173; [2] R. Chen, R. Poling-Skutvik, A. Nikoubashman, M. P. Howard, J. C. Conrad, and Jeremy C. Palmer, Macromolecules, 2018, 51, 1865-1872; [3] A. Malevanets and R. Kapral, J. Chem. Phys., 1999, 17, 8605-8613; [4] L.-H. Cai, S. Panyukov, and M. Rubinstein, Macromolecules, 2011, 44, 7853-7863.

Wednesday 6:30 Woodway II/III

PO43

### **Assembly of tripeptide hydrogels**

Lavenia J. Thursch<sup>1</sup>, Nicolas J. Alvarez<sup>1</sup>, David DiGuseppi<sup>2</sup>, and Reinhard Schweitzer-Stenner<sup>2</sup>

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We have discovered a unique series of tripeptides that form strong hydrogels. The hydrogels are composed of micron sized fibrils that are highly entangled and volume spanning. These hydrogels have potential in biomedical and drug delivery applications as they are inexpensive to synthesize and biocompatible. Previous studies found that the tripeptide glycylalanyl glycine in 55 mol% ethanol/45 mol% water forms a gel below a melting temperature of ca. 36C. This gel is of particular interest because it defies our current understanding of peptide aggregation mechanisms. This study aims to understand the consecutive formation of aggregates, fibrils and gel network using rheology, differential scanning calorimetry and x-ray scattering tools. We will investigate the impact of ethanol, peptide concentration, pH and temperature on the kinetics, structure and strength of the gel to improve aggregation models and to develop this novel material for drug delivery applications.

Wednesday 6:30 Woodway II/III

PO44

### **Gel formation in urethane liquid oligomers**

Praveen Agarwal<sup>1</sup>, Bob Sammler<sup>2</sup>, Asjad Shafi<sup>1</sup>, and Luigi Pellacani<sup>3</sup>

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Gel formation is a ubiquitous phenomenon for various materials including polymer solutions, ionomers, biomaterials, and consumer household products. Understanding the physical interactions that lead to gel formation is essential for rational material design and controlling the gel formation characteristics; hence is a topic of significant interest. We have investigated a gel formed in a urethane oligomer system dispersed in an organic solvent. Mechanism of gel formation was investigated by rheology, polarized optical microscopy and FTIR. We find evidence of hydrogen bonding and ordered structure formation in the gelled systems. Additionally, a rheology based technique was developed to screen formulations for gel formation.



Wednesday 6:30 Woodway II/III

PO45

**Rheological characterization of BDDE crosslinked hyaluronic acid gel for manufacturing quality control of the dermal filler: Steady shear flow and dynamic viscoelastic properties**Keyong Ho Lee<sup>1</sup>, Bokryul Choi<sup>2</sup>, E Sle Kim<sup>3</sup>, and Ju Hee Kang<sup>4</sup><sup>1</sup>R&D, Across co. Ltd., Chuncheon, Republic of Korea; <sup>2</sup>R&D, Across co. Ltd., Chuncheon, Republic of Korea; <sup>3</sup>R&D, Across co. Ltd., Chuncheon, Republic of Korea; <sup>4</sup>R&D, Across co. Ltd., Chuncheon, Republic of Korea

The purpose of this study is carried out to confirm that how much affect the differences of rheological properties of the raw material about manufacturing the crosslinked gel, which is used to the dermal filler for the medical device in the aesthetic field. In case of non-crosslinked HA, the shear thinning behavior can be clearly seen with viscosity decreasing as the shear rate is increased. Also, of interest here is that the sample tends to a Newtonian plateau with decreasing shear rate. The plateau viscosity, known as the zero-shear viscosity, is a useful and important material attribute, signifying the effective viscosity in an at rest condition. The crosslinking brings about a reduction of the intrinsic mobility of the polymer chains that are not able to release stress; consequently, the material shows a predominant elastic behavior ( $G' > G''$ ) and behaves as a three-dimensional network where the principal mode of accommodation of the applied stress is by network deformation. The decrease of Intrinsic viscosity of HA leads to gels with improved viscoelastic properties because the elastic modulus is proportional to the number of crosslinking points, that increase with the increasing of the amount of crosslinker. In crosslinked gels, it can be noticed that the elastic modulus is one order of magnitude higher than the viscous modulus,  $G'$  is almost independent of frequency and  $\tan \delta$  is in under 0.2. These samples behave as strong gel materials. These crosslinked gels exhibit a rheological behavior typical of a strong gel and show improved viscoelastic properties by increasing HA concentration and decreasing intrinsic viscosity. Therefore, the control of intrinsic viscosity of HA as raw material was a very important factor in the manufacture of crosslinked gel.

Wednesday 6:30 Woodway II/III

PO46

**Structure, dynamics and rheology of porous, low density colloidal gel electrolytes**Sanket R. Kadulkar, Debapriya Banerjee, Fardin Khabaz, Venkat Ganesan, Thomas M. Truskett, and Roger T. Bonnecaze  
*McKetta Jr. Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

Colloidal gels are considered to be a viable alternative to liquid electrolytes in batteries and energy storage systems due to their ability to provide thermal stability, mechanical strength and realize novels mechanisms to enhance ion conductivity. In this work, physical gels with an open, porous microstructure were obtained by competing attractive and repulsive interactions developed and optimized from inverse design studies. Colloids self-assemble into desired equilibrium microstructures of transient and arrested dynamics. Using small amplitude oscillatory shear (SAOS) simulations, rheology of these suspensions is probed from a coarse-grained framework assuming the polymer-solvent bulk matrix does not contribute significantly to rheology. Ion conductivity is also studied computationally for these gels by employing enhanced transport pathways on the surface of colloids as observed in recent experimental studies. Tuning the range of attractive and repulsive forces yields different transient and arrested microstructures such as percolated strings, bcc crystal with clusters of particles at lattice sites, bernal spiral configuration of colloids, etc. even at low packing fractions ( $\phi=0.1$ ). We show that certain gel structures exhibit better ion diffusivity as well as higher storage modulus in comparison to others demonstrating an interesting result bridging the trade-off between mechanical strength and ion conductivity due to altering the mechanism of ion transport from polymer segmental mobility to utilizing colloid surface in above colloidal gels. We also compare the particle-particle bond lifetime to the relaxation times obtained from the SAOS response for systems in the gelation boundary or close to gelation suggesting that bond breaking is the dominant factor affecting the SAOS response.

Wednesday 6:30 Woodway II/III

PO47

**Cure profile of highly filled silicone gel**Myoungbae Lee and Jeremy M. Beebe*Analytical Sciences, Core R&D, The Dow Chemical Company, Auburn, MI 48611, United States*

Rheological cure profile of elastomers/gels is commonly utilized in industry for curing kinetics study, quality control, and so on. Cure profile of a highly filled silicone gel was generated by utilizing appropriate testing conditions, e.g. strain amplitude within linear viscoelastic regime and below the onset of wall slip. While working to optimize the testing conditions, a unique property change pattern was observed from a highly filled silicone gel. The rheological properties of unfilled or lightly/moderately-filled materials change smoothly as curing proceeds. On the other hand, we observed that the cure profile of the highly-filled silicone gel exhibited large fluctuation of  $\pm 10$ -15% amplitude. Despite the large fluctuation, the cure profiles were very repeatable: the measurement variation was less than 2%, which is merely comparable to the variations of typical rheology tests of simple materials. This fluctuation disappeared when a strain above the onset of wall slip was used. This leads to the conjecture that the fluctuation is a reflection of physical contacts among filler particles and between the plates and filler particles. That is, the fluctuation could be an evidence of well-developed continuous pathways for conduction, which is a primary function of the highly filled gel. Also, an unexpected effect of rheometer plate type was observed. The above-mentioned characteristic cure profiles were obtained by using typical aluminum or tin disposable plates. However, the cure profiles generated with an inorganic-material-coated plate exhibited lower modulus and poor repeatability, which are believed to be signs of mild wall slip. Plate surface roughness of microscopic level and affinity between the filler particles and plate material will be discussed as possible influential factors.

Wednesday 6:30 Woodway II/III

PO48

**Polymer-nanoparticle hydrogels for biomedical applications**Hector Lopez Hernandez, Anthony C. Yu, Abigail K. Grosskopf, and Eric Appel  
*Stanford University, Stanford, CA, United States*

Interest and research in hydrogels have increased over the past 30 years for biological applications such as drug delivery, 3D printing bioinks, and cell therapies. They are readily suited for biological applications because they possess tissue-like mechanical properties, high water content, biocompatibility, and stimuli-responsiveness. Often, the desired rheological response of the hydrogels is constrained by the multiple stages required for successful administration, including processing, delivery, and terminal function. For example, injectable hydrogels for cell therapies must allow for facile mixing with cells, easy extrusion through high gauge needles, and retention of the cargo at the site of injection over the intended therapeutic time span. Here we present a full rheological characterization of polymer-nanoparticle (PNP) hydrogels that demonstrate tunable shear-thinning, yield stresses, and viscoelastic responses over a wide range by tuning the concentration, molecular weight, and relative ratios of polymer to nanoparticles. PNP hydrogels were created by simple mixing of polyethylene glycol-b-poly(lactic acid) nanoparticles with hydroxypropylmethylcellulose. We tuned the rheological response of the PNPs for applications which include fire-retardants, adhesion prevention barriers, and cell delivery. For cell delivery, the hydrogels were designed to shear thin, lowering the required pressure to inject a patient but retaining a cohesive localized depot after injection. In adhesion prevention barriers, we found that yield stress is correlated with the successful application of the barrier. Lastly, for fire-retardants, we demonstrate the ability to spray and deliver hydrogels with common spraying procedures, yet drastically increase the retention of fire-retardants onto target fuels over current formulations. We conclude that creating a more in-depth understanding of how to precisely tune the rheological properties of PNPs may provide a means for precisely creating a desired rheological response.

Wednesday 6:30 Woodway II/III

PO49

**Dense microgel suspensions with competing interaction potentials**Gaurav Chaudhary<sup>1</sup>, Ashesh Ghosh<sup>2</sup>, Kenneth Schweizer<sup>2</sup>, and Randy H. Ewoldt<sup>1</sup><sup>1</sup>*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States;* <sup>2</sup>*Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We investigate the linear and nonlinear rheology of soft thermoresponsive pNIPAM-microgel suspensions. By increasing concentration of the suspension, we observe a transition from a viscous liquid to an entropic glass to a soft jammed state at low temperatures when the microgels interact via a repulsive potential. Increasing the temperature of the suspension beyond the Lower Critical Solution Temperature [LCST], introduces additional attractive interactions. The competition between repulsive and attractive interactions leads to a rich temperature-dependent rheological response that is also concentration-dependent. We present a theoretical approach based on a nonlinear Langevin equation for Hertzian contacting spheres and Naïve Mode Coupling Theory (NMCT), which requires a non-trivial description of the effective particle size as a function of concentration and temperature, to understand the suspension dynamics in different regimes of temperature and concentration. The model captures the linear (shear moduli) and nonlinear (yield) properties of the soft particle suspension as a function of composition in the entropic glassy regime.

Wednesday 6:30 Woodway II/III

PO50

**Surfactant- versus pH-activated microgel suspensions**Sarah Goujard<sup>1</sup>, Clémentine Locatelli-Champagne<sup>2</sup>, Jean-Marc Suau<sup>2</sup>, and Michel Cloitre<sup>1</sup><sup>1</sup>*Soft Matter and Chemistry, ESPCI Paris, Paris 75005, France;* <sup>2</sup>*Coatex SAS, Genay 69730, France*

Stimuli-responsive microgels are submicrometer particles made of cross-linked polymeric networks that undergo a volume transition in response to changes in pH, temperature, or solvent quality. Since the volume fraction increases upon swelling, randomly close-packed suspensions with remarkable viscoplastic properties and optical transparency, are obtained at low polymer content. These features are exploited to design rheological modifiers used in cosmetics, pharmaceuticals, and food products.

Here, we trigger the swelling of microgels by the addition of surfactants, which interact with the polymeric network and induce swelling. We address this question for alkyl acrylate/methacrylic acid copolymers with different crosslink densities, which are mixed with ionic or neutral surfactants. The swelling ratio depends on the nature and concentration of the surfactant. Using a combination of techniques such as rheology, fluorescence, conductimetry and scattering experiments, we propose a mechanism that accounts for the swelling of the microgels when the surfactant concentration is increased. We build a rheological phase diagram, which in addition to the fluid and solid phases gives evidence for a reentrant transition reminiscent of that observed in attractive glasses. We discuss the rheological properties that characterize each phase. These results for surfactant-activated microgels are compared with the behavior of pH-triggered microgels.

Wednesday 6:30 Woodway II/III

PO51

**Structure of polyelectrolytes in length-mismatched coacervates**Amanda Marciel<sup>1</sup>, Samanvaya Srivastava<sup>2</sup>, and Matthew V. Tirrell<sup>1</sup><sup>1</sup>IME, University of Chicago, Chicago, IL 60637, United States; <sup>2</sup>Chemical and Biomolecular Engineering, University of California Los Angeles, Los Angeles, CA 90095, United States

We examined the effects of polyelectrolyte chain length on complexation behavior, polyelectrolyte conformation and rheological properties. We used charged homopolymer polypeptides - (poly)-lysine and (poly)-glutamic acid to prepare liquid coacervates with highly length mismatched conditions. This model system allows the chain length (6 - 800-mer), side-chain functionality and chirality (L, D) to be tuned precisely while keeping the backbone chemistry constant, thus enabling a systematic investigation of polyelectrolyte chain conformation in the liquid coacervate phase.

Wednesday 6:30 Woodway II/III

PO52

**Rheology of amine functionalised poly(cyclooctenes): Transition from liquid- to solid-like**Tanja Tomkovic<sup>1</sup>, Damon J. Gilmour<sup>2</sup>, Laurel L. Schafer<sup>2</sup>, and Savvas G. Hatzikiriakos<sup>1</sup><sup>1</sup>Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC V6T-1Z3, Canada; <sup>2</sup>Chemistry, The University of British Columbia, Vancouver, BC, Canada

Poly(cyclooctene) with secondary aryl-amine functionalities were synthesized using ring-opening metathesis polymerization combined with hydroaminoalkylation reaction. The resulting polymers were characterized by means of <sup>1</sup>H NMR and IR spectroscopies, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and solution and melt rheology. A plethora of distinctly different rheological behavior was obtained by controlling the molecular weight and by introducing various functionalities that exhibit different hydrogen bonding strengths. These novel materials reveal an evident transition from liquid- to solid-like behavior through gel formation. The detailed rheological study demonstrates the formation of the 3D network formed by physical crosslinking of hydrogen bonds.

Wednesday 6:30 Woodway II/III

PO53

**Phase behavior of block copolymer Pluronic: A rheological perspective**Khushboo Suman, Sagar Sourav, and Yogesh M. Joshi*Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India*

We study temperature induced phase change of a block copolymer polyoxyethylene-polyoxypropylene-polyoxyethylene (PEO<sub>100</sub>-PPO<sub>65</sub>-PEO<sub>100</sub>, Pluronic F127) having a concentration in a range: 20 weight% to 35 weight %. While this temperature dependent phase change visually appears like a liquid-soft solid transition, and the soft solid state has been termed as gel in the literature, there is a debate regarding precise microstructure of the soft solid state. In this work, we carry out frequency sweep at various temperatures on F127 solution on different days since preparation of a solution. We observe that irrespective of the concentration in the explored range, an aqueous solution of F127 shows all the rheological characteristic features of sol - gel - glass transition. Such behavior suggests the transition of a liquid-like sample to a space spanning percolated network, whose rheological characteristic is increase in  $\tan \delta$  with frequency, followed by a glassy transition as characterized by a peak in  $\tan \delta$ . Interestingly, the maxima in  $\tan \delta$  shifts to lower temperatures with an increase in frequency, which illustrates the rate dependence of glass transition. The temperature at which the glass transition is observed decreases with increase in the concentration of F127. The glass transition behavior is also observed at higher temperature during gel melting. Dynamic light scattering has been employed to study the evolution of micellar radius with temperature in F127 solution. We also estimate heat of gelation associated with F127 solution and find it to be in close agreement with the values reported in the literature. Finally, based on the rheological studies we construct a phase diagram and discuss the similarities and differences with respect to various phase diagrams of F127 solution available in the literature.

Wednesday 6:30 Woodway II/III

PO55

**Studying the polymerization kinetics in nano-confined structures using chemorheology**Sahar Qavi, Alireza Bandegi, and Reza Foudazi*Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*

Block copolymers self-assemble in the presence of solvents and produce nano-scale structures such as lamellar, normal, and reverse hexagonal also known as lyotropic liquid crystals (LLCs). Mesoporous organic materials can be made through mesophase templating. This work describes the kinetics of thermal polymerization in nano-confined structures of mesophase templates using chemorheological studies. A set of isothermal time sweep tests at three different temperatures is performed on mesophases to discern the polymerization rate and reaction constants. We have fixed the concentration of monomeric phase in lamellar and hexagonal phases while retaining the structure during thermal polymerization at elevated temperatures. The obtained mesoporous structures have domain sizes comparable to that of mesophases before polymerization. We found that the type of mesostructure strongly influences the polymerization kinetics. The fastest polymerization rate occurs in reverse hexagonal mesophases due to high local monomer concentration and depression of termination rates. In lamellar nanoconfinement, the polymerization rate is higher than bulk polymerization, but lower than the reverse hexagonal confinement. Differential scanning calorimetry at elevated temperatures confirms the obtained results from chemorheology.

Wednesday 6:30 Woodway II/III

PO56

**Energetics of magnetically tunable colloidal assembly in quasi two dimensions**Elaa Hilou and Sibani Lisa Biswal*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

We use rotational magnetic fields to assemble superparamagnetic beads into colloidal droplets that crystallize as we increase the field strength applied. The interaction potential between a particle pair is similar to that of the Lennard-Jones potential, but with a longer attractive term and a tunable well-depth. At intermediate field strengths, the formed clusters exhibit both liquid and crystalline like behaviors, which are characterized by examining their morphology as well as their energetic properties by measuring the bond orientation order parameter, density, and excess potential energy as we move from the bulk of the cluster to the interfacial layer. The change in the interaction also causes a change in the interfacial stiffness, which can be directly measured by applying a Fourier expansion on the interfacial fluctuations. Our analysis focuses on the quasi-equilibrium state as well as the aggregation dynamics such as coalescence. By manipulation of the particle-particle interactions, one can use the system as a model to study material properties at the atomic scale.

Wednesday 6:30 Woodway II/III

PO57

**Actuation of dynamic structures in paramagnetic colloidal chains**Steve Kuei and Sibani Lisa Biswal*Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

The deformation of semi-flexible filaments in response to external forces and their surrounding fluid leads to a host of different dynamical responses, ranging from simple rotary orbits to complicated non-reciprocal orbits; controllable actuation of these modes has significant potential for application in microfluidic scale propulsion, fluid manipulation, and biomimetic systems. Various forces act along the length of the filament, with external driving forces offset by hydrodynamic drag and elastic restoration, and it is the competition between these forces that generate rich dynamics. We synthesize paramagnetic colloidal particle chains, and then utilize a rotating magnetic field as an external force, with which we are able to experimentally probe the various dynamical regimes. In particular, we focus on two regimes where the chains beat with a periodic deformation, and where the chains form tightly wrapped coils. By complementing our studies with Brownian dynamics simulations, we elucidate and work towards optimizing fiber dynamics as a function of the dimensionless Mason and magnetoelastic numbers, which encompass the tunable parameters of our system.

Wednesday 6:30 Woodway II/III

PO58

**Desiccation cracks and external field-induced directed assembly of colloids**Hisay Lama<sup>1</sup>, Madivala G. Basavaraj<sup>2</sup>, and Dillip K. Satapathy<sup>3</sup>*<sup>1</sup>Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India; <sup>2</sup>Chemical Engineering, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India; <sup>3</sup>Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India*

Desiccation cracks are ubiquitous and are commonly observed in the dried mud, old paintings, and colloidal crystals. These cracks manifest itself in various morphologies such as polygonal patches, spiral, linear stripes etc., and exhibits self-similarity. For several decades, colloids were used as a model system to study various features found in desiccation cracks and it was commonly understood that the cracks occur due to the release of excess stress energy which is accumulated during desiccation. However, the source of various crack morphologies is still not completely understood. We perform an experimental study to investigate the origin of different crack morphologies that occurs via desiccation. In typical experiments, a colloidal dispersion consisting of ellipsoid particles of different aspect ratios were allowed to evaporate freely and the cracks pattern were monitored in the dried residue. Our experimental finding reveals that the crack morphology is highly dependent on the shape and the microstructural arrangement of the particles. In addition, we develop a novel strategy to control the crack pattern by controlling the microstructural arrangement of particles using an external field such as magnetic field, electric field or thermal field. The application of an external field facilitates the generation of long-range quasi-periodic cracks which can be useful for various technological applications such as fabrication of lithographic templates.

Wednesday 6:30 Woodway II/III

PO59

**Rheological evaluation of suspensions after gap positioning using different squeeze velocity: Influence of solid content and fluid viscosity**Roberto Cesar de O. Romano, Marcel H. Maciel, Daniele de Lima T. Pessutto, Heitor M. Bernardo, Gabriela S. Soares, and Rafael G. Pileggi*Civil Construction Engineering, University of São Paulo, São Paulo, São Paulo 61548, Brazil*

Parallel-plate rheometry is a common configuration used to evaluate Portland cement or supplementary cementitious materials due, mainly, the rheological characteristics of suspensions. However, to carry on the tests with a precise methodology or to evaluate correctly the rheological parameters, the stage of sample preparation is very important. In this work, a rheological investigation regarding the influence of squeeze velocity to gap positioning to prepare the samples for rotational rheometry was performed. The normal force and the shear stress obtained were analyzed in function of squeeze velocity and solid content of each suspension. A limestone filler and silicon fluid with viscosities of 10cSt or 1000cSt were the materials used. Pastes were prepared with three different solid content (10, 40 and 80%-in weight). The pastes were evaluated using a stainless

steel parallel-plate geometry and a compressive rheometry tests were carried out using different squeeze velocity (0.3, 1.25 or 2.5 mm/min), followed by the stepped flow test. The squeeze velocity causes phase separation, which was more intense in the suspensions of fluid with lower viscosity, but this phenomenon was attenuated in function of increasing solid content. Consequently, the results obtained in the rotational rheometry were affected. Hence, if this experimental parameter is neglected and phase separation occurs, the subsequent shear rheological parameters measured may be overestimated, inducing incorrect conclusions. So, the development of experimental protocols for the evaluation of pastes using parallel-plate rheometry needs to be better understood, considering the mix design to prepare pastes, squeeze condition to prepare the sample, and precise choice of shear method, to avoid inaccuracies in the determination of rheological parameters with practical interest. This is extremely important, because in case of application of rheological models, the correlation with real data just will be correct if the tests were performed in an adequate way.

Wednesday 6:30 Woodway II/III

PO60

### **Exploring anisotropic response in Magneto-Rheological fluids under shear and compressive deformation**

David Bohnsack<sup>1</sup>, Carlos Gracia-Fernández<sup>2</sup>, and Modesto T. Lopez-Lopez<sup>3</sup>

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Magneto-Rheological (MR) fluids are smart materials that can transition in a controlled and reversible manner from a liquid to a solid-like material in the presence of an external magnetic field. In the absence of magnetic fields, the rheology of MR fluids exhibits suspension-like thixotropy. On exposure to an external magnetic field, the highly magnetizable particles in the fluid align along the field to form flocculated clusters within milliseconds. This rapid response to magnetic field application changes the bulk rheological properties, providing a simple means to tailor fluid characteristics such as yield stress and viscosity through the magnetic field strength. Considerable research effort on MR fluids has focused on characterizing the rheology of MR fluids in the shear direction. However, to further our understanding of these materials in the as-used orientation, it is critical to investigate them in the compression direction as well. In this work, we report on the magneto-rheological properties of a carbonyl-iron suspension as a function of magnetic field intensity in both the shear and compression orientation. Two different MR fluids were studied on a TA Instruments DHR-3 rheometer equipped with a Magneto-Rheology accessory that is capable of real-time closed loop magnetic field control. The DHR's unique ability to do Dynamic Mechanical Analysis (DMA) measurements under shear and compression in the presence of magnetic fields allowed the quantification of field-strength driven microstructural orientation in both directions. The commercially available MR fluid displayed a pronounced difference between the compressive and shear moduli across the entire range of field strengths. However, our results demonstrate that it is possible to formulate MR fluids that have isotropic material properties in both directions to achieve a uniform field-induced response. The effects of particle volume fraction and viscosity of the carrier fluid on the MR fluid's tunability are discussed.

Wednesday 6:30 Woodway II/III

PO61

### **Numerical investigation of viscoelastic instabilities using an improved Level-Set method**

Artur Sucena<sup>1</sup>, Manuel A. Alves<sup>2</sup>, Fernando T. Pinho<sup>1</sup>, and Alexandre M. Afonso<sup>1</sup>

<sup>1</sup>Departamento de Engenharia Mecânica, FEUP CEFT, Porto 4200-465, Portugal; <sup>2</sup>Departamento de Engenharia Química, FEUP CEFT, Porto 4200-465, Portugal

Viscoelastic fluids behave differently from Newtonian fluids in many flow conditions, and in particular there are specific instabilities, such as the low Reynolds number helical extrudate instability, observed experimentally in an extrudate of viscoelastic fluid [1]. This instability is here investigated numerically using an improved version of the Level-Set method [2], implemented in an in-house solver using the Finite-Volume Method. In the Level-Set method, the interface is represented by a curve using the so-called level-set function, which is defined as the signed distance to the interface. This function is governed by a Hamilton-Jacobi partial differential equation particularly suitable for the simulation of changing topologies and solved numerically. The code uses a new resistance scheme [3] to preserve the definition of the level-set function along with a new computationally efficient mass correction method [4]. These two methods improve the precision of the interface description between two flows without significantly increasing the computational effort of the solver, allowing the use of more refined meshes.

Wednesday 6:30 Woodway II/III

PO62

### **Detection of time dependent response of thixotropic systems by analysis of SAOS using Kramers-Kronig relations**

Koduvayur A. Ramya, Ramanathan Srinivasan, and Abhijit P. Deshpande

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Microstructural evolution and aging are inherently associated with thixotropic materials. A thorough understanding of such processes is essential in handling the systems due to the varied response time scales involved. The effect of these time dependent phenomena on rheological measurements was investigated in this work using Kramers-Kronig relations. Thixotropy was probed by analysing small amplitude oscillatory shear (SAOS) response of an experimental suspension as well as of corresponding constitutive equations. A model thixotropic suspension of fumed silica in paraffin oil / polyisobutylene [J. Non-Newtonian Fluid Mech. 139(1-2), 21-30 (2006); Rheol. Acta 45, 23-32 (2005)] was reformulated and characterized using different measurement conditions. To capture the response, phenomenological models based on structure kinetics approach are evaluated. The experimental and simulated data set obtained from oscillatory shear are subjected to Kramers-Kronig (KK) transforms based on a method proposed by B. A. Boukamp [Solid State Ionics 169 [1-4] 65-73 (2004); J. Electrochem. Soc. 142 [6] (1995) 1885-1894]. This method checks for KK compliance, if compliance is observed, the data can be said to be from a stable, causal, and linear system. In particular, a thixotropic fluid will exhibit structural response in the sense that upon removal of applied perturbation the system would not quickly

revert to the original condition. Any deviations from KK compliance can be assigned to nonlinearity, non-causality and/or instability. In case where small signals are employed such as in SAOS, nonlinearity can be ruled out and structural response, for example arising from thixotropy, can be identified.

Wednesday 6:30 Woodway II/III

PO63

### **Instability of shear thinning pressure driven channel flow**

Hugh J. Barlow<sup>1</sup>, Ewan J. Hemingway<sup>1</sup>, Andrew Clarke<sup>2</sup>, and Suzanne M. Fielding<sup>1</sup>

<sup>1</sup>Physics Department, South Road, Durham University, Durham, Durham DH1 2DP, United Kingdom; <sup>2</sup>Schlumberger Cambridge Research Centre, Cambridge, United Kingdom

We examine the instability of shear-thinning pressure-driven channel flow to undulations with wavevector in the flow direction. By means of linear stability analysis and full nonlinear simulations across a suite of commonly used constitutive models, including the microscopically motivated Rolie-Poly model of linear entangled polymers and the phenomenological Johnson-Segalman, we demonstrate the instability to be rather generic across shear thinning fluids. This finding is consistent with the original predictions of [1] in the context of the White-Metzner model, and with recent experiments [2,3,4]. We show that the onset of instability can be fitted using a generic functional form that indicates that the instability is driven by gradients in normal stresses within the channel, combined with the shear thinning properties of the fluid.

[1] Helen J Wilson and John M Rallison. JNNFM, 87, 75-96, 1999. [2] H. Bodiguel, J. Beaumont, A. Machado, L. Martinie, H. Kellay, and A. Colin. PRL, 114, 028302, 2015. [3] RJ Poole. Phys. Rev. Fluids, 1, 041301, 2016. [4] L. Picaut, O. Ronsin, C. Caroli, and T. Baumberger. Phys. Rev. Fluids, 2, 083303, Aug 2017.

Wednesday 6:30 Woodway II/III

PO64

### **Viscous fingering of a draining suspension**

Yun Chen<sup>1</sup>, Frank Malambri<sup>2</sup>, and Sungyon Lee<sup>1</sup>

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The drainage of liquid is a commonplace process that affects a wide array of industrial applications ranging from medical procedures, manufacturing processes to food processing. While many drainage-related applications involve the complex fluids comprising solid particles, the effects of suspended particles on the liquid drainage have not been considered, leaving simple fundamental questions on the suspension drainage unanswered. In this work, we experimentally investigate the effects of non-colloidal particles on drainage by withdrawing suspensions from an air-filled Hele-Shaw cell in a radial sink flow. As expected, the Saffman-Taylor viscous fingering arises as air invades a draining viscous suspension. Despite seminal works on viscous fingering, only a few have studied this “inward” viscous fingering for pure liquids and none for suspensions. We find that, while the overall behavior of fingering remains unchanged from the pure liquid case, suspended particles are shown to delay the onset of fingering but also to accelerate its growth rate. This surprising dual effect of particles results in the increase of the total drainage time and in the amount of drained suspension as a function of particle concentrations. In addition, the particle entrainment into the thin film of wetting oil causes particles with select sizes to remain on the channel walls instead of draining, which closely follows our simple theoretical prediction.

Wednesday 6:30 Woodway II/III

PO65

### **Record of rheology: Documenting past Bingham Medal winners**

Mikayla L. Cleaver

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The year 2029 will be the 100th Anniversary of the founding of the Society of Rheology. In preparation for the centenary, I have been compiling precise and engaging biographies of past Bingham Medal winners to be uploaded to the Society of Rheology webpage, as well as to the Physics History Network on the American Institute of Physics (AIP) website. I have also been promoting higher engagement with the members of the society through the use of social media via the Niels Bohr Library and Archives (NBLA) Facebook and Twitter. Why is it important to do this? Studying the history of science allows us to learn about the great men and women in science and their accomplishments that moved the scientific community forward. This project will help preserve the history of the Society of Rheology for future generations of members.

Wednesday 6:30 Woodway II/III

PO66

### **CFD simulation of the extrusion process in the fused deposition modeling using a viscoelastic model**

Behrouz Behdani<sup>1</sup>, Leah Mason<sup>2</sup>, Ming Leu<sup>2</sup>, and Joontaek Park<sup>1</sup>

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<sup>2</sup>Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, MO 65409, United States

Fused Deposition Modeling (FDM) is the one of the most common additive manufacturing techniques. FDM builds a 3D object by extruding strands of polymer melts, layer by layer, on a platform. Despite extensive experimental studies on FDM process, numerical modeling of these systems, particularly for viscoelastic polymer melts, is yet to be done. Many issues related to FDM like surface roughness and die swell are originated from the viscoelastic behavior of polymer melts. In present work, 3D CFD simulation of the extrusion-based process is performed based on the Finite Volume Method. The polymer melt is simulated as a Newtonian and a viscoelastic fluid. Oldroyd-B model, one of the most

common models for viscoelastic fluids, is used to predict the viscoelastic behavior of the polymer melt. The effects of geometrical parameters (e.g. cross section shape and area) and the flow characteristics (e.g. nozzle and moving substrate velocities) on the deposition of layers on the moving substrate are investigated. Additionally, the results for thickness of the extruded strands have been related to dimensionless number of the systems (i.e.  $Re$  and  $Wi$ ). The results from both the Newtonian and the viscoelastic fluid simulations are also compared with experimental results. For experimental investigation, Acrylonitrile Butadiene Styrene (ABS) filaments are utilized for extrusion in Prusa 3D printer. Results prove significant impacts of gap between plate and nozzle and the ratio of nozzle velocity to substrate velocity on the thickness and width of extruded layers. Moreover, if the surface tension effect is neglected, melt profile after extrusion is similar in processes with the same Reynolds number.

Wednesday 6:30 Woodway II/III

PO67

### **Shear banding and delayed yielding in thixotropic yield stress fluids**

Mayank Agarwal, Lakshmi Kushwaha, Yogesh M. Joshi, and V Shankar

*Chemical Engineering, Indian Institute of Technology Kanpur, KANPUR, UTTAR PRADESH 208016, India*

In this work, we investigate the shear banding and delayed yielding in the thixotropic yield stress fluids experimentally and with the numerical solution of a simple fluidity model. We perform creep experiments on Ludox gel (an aqueous suspension of charged colloidal particles) for stresses above and below the yield stress. We observe an increase in yield stress and delayed yielding as we increase the waiting time after shear rejuvenation. The timescale at which yielding starts in material decreases with the difference between the stress and the yield stress as the power law. Then we study the transient response of the Couette flow subjected to step stress using fluidity model proposed by Coussot et al., 2002. We observe that the inclusion of inertia has a significant influence on the existence of the transient as well as steady state shear bands. For non-monotonic flow curves, the system shows transient and/or apparent steady-state shear banding only for zero waiting time. On the other hand, for monotonic flow curve, the system does not show the presence of shear banding. Furthermore, irrespective of the nature of flow curves, sufficiently aged samples (non-zero waiting time) show the presence of delayed yielding. The experimental results are in good agreement with simulations.

Wednesday 6:30 Woodway II/III

PO69

### **Evolution of shear bands in Carbopol gel under transient and oscillatory shear**

Yufei Wei<sup>1</sup>, Luofu Liu<sup>2</sup>, Michael J. Solomon<sup>1</sup>, and Ronald G. Larson<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States;* <sup>2</sup>*School of Chemistry, Beihang University, Haidian Dist, Beijing 100191, China*

Shear banding often occurs in yield-stress materials and greatly alters the flow field as well as the bulk rheological properties. Understanding the onset and evolution of shear bands is crucial to correctly interpreting the rheological response of yield-stress materials and is important in the design of processing flows that enhance or mitigate shear banding as needed. This poster presents our experimental results of rheological tests and the simultaneous velocimetry measurement. The testing material is a Carbopol gel, a model yield-stress fluid, seeded with fluorescent tracer particles for particle image velocimetry. The rheological experiments include shear startup tests, flow reversal tests, and large amplitude oscillatory shear (LAOS) tests. We used a parallel plate geometry with rough surfaces to prevent wall-slip. We calculated the degree of banding (DOB) based on the results of time-resolved velocimetry. We found that upon shear startup, the DOB increases, reaches an overshoot, and then gradually decays towards a plateau. The overshoot of the DOB typically occurs shortly after the stress overshoot, but shear banding starts before the stress overshoot is reached. The banded flow becomes uniform if the shearing direction is suddenly changed. Shear bands gradually develop after shear reversal. In LAOS tests, as the amplitude increases, shear bands occur along with the emergence of a nonlinear rheological response. For large amplitudes, the DOB exhibits a hysteresis loop when plotted versus shear strain or shear rate. We examine the experiments in light of recent theoretical studies.

Wednesday 6:30 Woodway II/III

PO70

### **Influence of the materials of the walls on the slip behavior of a microgel in Couette flow as studied by PIV**

Esteban F. Medina-Bañuelos<sup>1</sup>, Benjamín M. Marín-Santibáñez<sup>1</sup>, and José Pérez-González<sup>2</sup>

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In this work, the flow kinematics of a model yield-stress fluid, a Carbopol 940 hydrogel, in a Couette cell with slip at the walls was analyzed under steady and laminar flow conditions by using the particle image velocimetry technique. The inner and outer cylinders were made up of hydrophobic and hydrophilic materials, respectively, to study the surface effect on the slip behavior of the hydrogel. The obtained velocity profiles evidenced the viscoplastic behavior of the hydrogel as rigid body-like motion across the gap for stresses below the yield value. Above the yield value, the fluid showed rigid body-like motion and shear flow partially in the gap, as well as pure shear flow once the shear stress at the outer cylinder surpassed the yield stress. Slip occurred at both cylinders for all the flow conditions and the slip velocity values increased along with the wall shear stress, but followed different trends due to differences in hydrophobicity of the surfaces of the cylinders. Finally, the yield stress was calculated with good accuracy from the velocity profiles and these were utilized to test a numerical solution to describe the flow kinematics of Herschel-Bulkley fluids in Couette flow without slip.

Wednesday 6:30 Woodway II/III

PO71

**Electroviscous effects on rheological properties of polymerized ionic liquids in ion condensed solutions**Atsushi Matsumoto<sup>1</sup>, Francesco Del Giudice<sup>2</sup>, Rachapun Rotrattanadumrong<sup>1</sup>, and Amy Q. Shen<sup>1</sup><sup>1</sup>Okinawa Institute of Science and Technology Graduate Univers, Onna, Japan; <sup>2</sup>Systems and Process Engineering Centre, College of Engineeri, Swansea University, Swansea, United Kingdom

We observed that rheological properties of a polymerized ionic liquid (PIL) in a mixture of an ionic liquid and a salt-free solvent did not follow the scaling laws for polyelectrolyte solutions proposed by Dobrynin et al. [1], especially at higher ionic liquid concentration  $c_s$ . Both specific viscosity  $\eta_{sp}$  and the longest relaxation time  $\lambda$  at a fixed polymer concentration were initially constants, but decreased with increasing  $c_s$  at  $c_s < 0.1$  M, consistent with the scaling prediction. However, when  $0.1 \text{ M} < c_s < 1.0 \text{ M}$ , both  $\eta_{sp}$  and  $\lambda$  exhibited slower reduction rate than those predicted. At  $c_s > 1$  M, the values of  $\eta_{sp}$  and  $\lambda$  increased with increasing  $c_s$ , independent of the polymer concentration. To understand this unusual rheological behavior, we introduce an alternative relaxation time  $\lambda^*$  which allows us to extract the contribution of the chain shrinkage on  $\lambda$  of the PIL solution. For dilute PIL solutions, the values of  $\lambda^*$  monotonically decreased with  $c_s$ , indicating that the chain size of PIL decreases with increasing  $c_s$ . On the other hand, the hydrodynamic radius (estimated by using dynamic light scattering) increased with increasing  $c_s$  at  $c_s > 1$  M. This result indicates that there is a relatively large ionic cloud moving together with a polyelectrolyte chain, implying that the distortion of ions, so-called the electroviscous effects, gives rise to additional energy dissipation, which leads to an increase in the viscosity of PIL solutions at higher concentrations of ionic liquid. Our findings demonstrate that rheological properties of PIL in ion condensed solutions are not only determined by the polymer dynamics.

[1] Dobrynin, et al., *Macromolecules*, 1995.

Wednesday 6:30 Woodway II/III

PO72

**Describing thixotropy with continuous spectra and low-dimensional metrics**Samya Sen and Randy H. Ewoldt*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We propose a continuous distribution of timescales to describe thixotropic breakdown and recovery after a step change in shear rate. These descriptions can be used like material functions, independent of any assumed underlying predictive thixotropic constitutive equation. The mathematical paradigm is similar to that of continuous viscoelastic spectra, but thixotropic spectral strengths are in terms of stress contributions (rather than modulus or viscosity spectra used for viscoelasticity) and depend on the initial and final shear rates imposed. Deconvolution with superposed viscoelasticity is considered. Thixotropic spectra can be represented by many discrete modes, but we demonstrate the value of parameterizing the shape of the thixotropic spectrum with an assumed functional shape using only a few parameters. Bayesian information metrics are used to identify the most credible model, which is a balance of goodness of fit and having a small number of parameters. We compare several functional forms (e.g. log-normal and Gumbel type distributions) along with simple cases including the single exponential and stretched exponential models. We show that for most material systems, an assumed distribution can fit the data at least as well as any commonly used form, and that for some materials, the fits are significantly better. An important outcome of this work is that one can easily derive low-dimensional descriptions from the timescale distribution including characteristic timescales (weighted averages), polydispersity of timescales, and total strength of thixotropic change. We use these low-dimensional parameters in plotting "Ashby-style" property diagrams that help compare various thixotropic materials. This is useful in applications where thixotropic properties may be critically important, such as droplet impact, splashing, and spray coating.

Wednesday 6:30 Woodway II/III

PO73

**Tunability and dark curing of photopolymerizable ionic liquids**Ria D. Corder, Sumner C. Dudick, and Saad A. Khan*Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

Ionic liquids pose a novel and tunable medium for bulk polymerization of vinyl monomers. 1-vinylimidazole displays intriguing viscosity growth trends when mixed with lithium bistriflimide salt to form an ionic liquid and then polymerized via a free-radical mechanism. Previous work has shown that increasing salt concentrations result in faster chemical conversion of monomer during photopolymerization. The purpose of our study is to determine how differences in kinetics are manifested in the development of material properties. This system does not crosslink or gel; rather, polymerization causes large increases in complex viscosity due to the formation of entangled polymer chains below the glass transition temperature. Dynamic oscillatory rheology was used to non-invasively measure complex viscosity during in-situ synthesis of poly(vinylimidazole.) We varied the salt concentration, ultraviolet (UV) light intensity, and UV exposure time and observed the effects on complex viscosity over time. We demonstrate that the complex viscosity of photopolymerized ionic liquids can be tuned by varying the salt concentration and UV dosage. As expected, samples exposed to higher UV dosages increase in viscosity more quickly and reach higher terminal viscosities. Unexpectedly, we observe that samples increase in viscosity most quickly at intermediate salt concentrations, which contradicts the chemical conversion trend. Another unexpected result is that the system exhibits dark curing, where samples continue to increase in viscosity after cessation of UV exposure. The extent of dark curing is also shown to be dependent on salt concentration. Electron paramagnetic resonance spectroscopy performed on a similar photopolymerizing system demonstrates that lithium salts can complex with and stabilize propagating radicals, which helps to explain our observations. We discuss potential mechanisms underlying the system dynamics and plan to incorporate additional approaches, such as photocalorimetry, to further understand the observed trends.



Wednesday 6:30 Woodway II/III

PO74

**Elastic stress during stepwise reduction in shear rate for thixotropic suspension**Jiho Choi and Simon A. Rogers*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

A comprehensive series of time-resolved stress jump tests is performed on a thixotropic fumed silica suspension to determine elastic contributions to thixotropic behaviors. The series of stress jumps tests is the most complete performed to date, encompassing jumps between three well-defined flow states, as well as flow reversals. We employ an experimental technique for measuring the elastic stress [1] in which flow is abruptly stopped. The elastic stress is identified via an extrapolation back to the moment of flow cessation. The elastic stress is measured across a range of shear rates, and during the transient response to a jump from one rate to another, providing a detailed data set that shows the importance of elasticity in thixotropy. It is shown that the evolution of the elastic stress closely follows that of total stress in the series of stress jump tests, indicating that elasticity is a significant contributor to thixotropy. The elastic stress is also calculated via the integration of a sequence of physical processes (SPP) [2] metric obtained from parallel superposition tests. The elastic stress calculated by integration of the SPP metrics matches the values measured via the stress jumps, but is obtained in a small fraction of the time required for full experimental discovery. These results highlight the utility of the SPP approach, which has so far been limited to LAOS studies only, in the study of thixotropy, and also indicate the importance of elasticity in thixotropy.

[1] Dullaert, K., and J. Mewis, "Stress jumps on weakly flocculated dispersions: Steady state and transient results," *J. Colloid and Interface Science*. 287, 542-551 (2005). [2] Rogers, S. A., "In search of physical meaning: defining transient parameters for nonlinear viscoelasticity," *Rheol. Acta*. 56, 501-525 (2017).

Wednesday 6:30 Woodway II/III

PO75

**Flow-visualization of concentrated surfactant paste: Elucidating flow field of complex fluids under shear deformation**Eduard A. Caicedo-Casso<sup>1</sup>, Kendra Erk<sup>2</sup>, and Seth Lindberg<sup>3</sup>*<sup>1</sup>MSE, Purdue University, West Lafayette, IN 47907, United States; <sup>2</sup>Materials Engineering, Purdue University, West Lafayette, IN 47906, United States; <sup>3</sup>Procter and Gamble, West Chester, OH 45069, United States*

Beauty care corporate engineers rely on shear rheology data of complex fluids to solve the daily issues. Complex fluids depict hydrodynamic instabilities which complicates the validation of data. Shear rheometers are partially unable to identify hydrodynamic instabilities, misleading an apparent trustable data set. To accurately measure rheological behavior, it is primordial to fully understand the fluid dynamics of the system. This understanding comes from elucidating the velocity field of the fluid under deformation. Non-intrusive visualization techniques with temporal and spatial capabilities are most adequate in this case. Dilute surfactant systems are vastly studied. However, few information is found in surfactant paste. Concentrated paste needs to be diluted, mixed and transported away. Consequently, a smooth processing and a profitable end-product requires a good rheology of raw materials. At present, the effect of shear deformation and salt content over the viscoelastic behavior of a commercially available anionic surfactant paste is evaluated. Shear rheometry coupled with ultrasonic speckle velocimetry (USV) is used to identify any hydrodynamic instabilities and their critical shear rates. A built-in-place ultrasonic visualization technique uses on a high frequency speckle signal. An Anton Paar 302 rheometer with a PMMA concentric cylinder fixture is used to impart different shear rates. The results show the existence of a critical shear rate below which the concentrated surfactant paste flow under a plug-flow behavior. Increasing shear rates produce the transition from plug-flow to shear bands. An apparent wall slip congruent to the applied shear rate is also observed.

Wednesday 6:30 Woodway II/III

PO76

**The effect of shear thinning of coating liquids on coating bead dynamics and operability coating window in dual-slot die coating flows**Jin Seok Park, Tae Hyung Yoo, and Hyun Wook Jung*Department of Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea*

Slot coating process is a promising method to produce uniform and thin layer of liquid film over the substrate at high speeds. This method has been usefully applied in various coating industries, including flat-panel display films, Li-ion secondary batteries, and fuel/solar cells. For the enhanced coating product quality and time/energy savings, recently, coating liquids are simultaneously deposited layer-by-layer over the substrate for multi-layer coating films via multi-layer coating processes. In these systems, it is important to understand flow dynamics in the coating bead region of multi-layer slot coating and establish operating parameters for uniform coating layers free from bead breakup and leaking. In this study, coating bead dynamics and operability coating windows of Carreau-type (shear-thinning) coating liquids are investigated in dual-layer slot die coating systems, employing the simplified viscocapillary and two-dimensional (2-D) CFD models. The effects of flow rate ratio between the top and bottom layers and their fluid properties are mainly considered. The viscocapillary model derived from 2-D full equations reasonably provides the position of the upstream meniscus, which is a key indicator to determine onsets for leaking and bead breakup, and the pressure distribution in coating bead region. Various results from the viscocapillary model are compared with those from 2-D CFD model.

Wednesday 6:30 Woodway II/III

PO77

**Additively manufactured vanes with modified geometries for measurements of yield-stress fluids**

Crystal E. Owens, Thaneer Narayanan, A. John Hart, and Gareth H. McKinley

*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

We constructed vanes with typical and novel geometries for rheological measurements using stereolithographic (SLA) 3D printing (Form2, Formlabs Inc), which works by UV-crosslinking a methacrylate-based liquid photopolymer to build a solid object layer by layer. The SLA printing process permits straightforward creation of complex structures with dimensional resolution  $<200\mu\text{m}$  over several cm in length, from materials having wide chemical compatibility and high mechanical stability. In particular, we designed a series of vane geometries for measuring the yield stress and flow curves of complex fluids that exhibit a yield stress, and demonstrated their use with viscous Newtonian fluids, carbopol-based hair gel, and a jammed emulsion (mayonnaise). In addition, the low cost of production allows these vanes to be disposable for measurement of caustic materials such as battery slurries.

Enabled by the SLA process, we introduce novel geometries designed to improve the typical 4-armed vane by creating a more homogeneous shear profile in the unknown test material, with minimally displaced sample material when inserting the vane. Geometries include a fractal structure, a hollow ribbed cylinder, and vanes with an arbitrary number of arms. The end of each vane connects to the spindle of a rheometer (Discovery Hybrid, TA Instruments) via an M4 helicoil threaded insert, resulting in a diameter runout of 0.1 to 1.0 mm without further processing. A 3D printed cup with a ribbed inner surface holds the sample fluid, and disassembles for ease of cleaning.

Finally, we designed and compared conversion equations that translate measured torque to material shear stress as a function of the vane geometry, and measured viscosity of silicone oils to within 5% for all vanes. We reproduced material flow curves with mean average error below 2% when compared to baseline flow curves measured by a cone and plate geometry, showing ultimately that the designs are useful for experiments, and not just made in vane.

Wednesday 6:30 Woodway II/III

PO78

**Multilamellar vesicle formation under large amplitude oscillatory shear**Stefan Kuczera<sup>1</sup>, Luigi Gentile<sup>1</sup>, Timothy I. Brox<sup>2</sup>, Ulf Olsson<sup>1</sup>, Claudia Schmidt<sup>3</sup>, and Petrik Galvosas<sup>2</sup><sup>1</sup>Lund University, Lund, Sweden; <sup>2</sup>Victoria University of Wellington, Wellington, New Zealand; <sup>3</sup>Paderborn University, Paderborn, Germany

Lyotropic lamellar systems exhibit intriguing shear-induced structural changes and a rich phase behaviour. For these materials continuous shear may induce the formation of multilamellar vesicles (MLVs) which is a defect structure resembling close packed spheres consisting of many concentric spherical bilayer shells (often referred to as “onions”) [1]. In this work we employ Rheo-NMR and Rheo-SALS which are established as complementary methods to conventional rheology. They provide localised and/or microscopic information of the fluid under shear [2,3].

Here we report on the application of Large Amplitude Oscillatory Shear (LAOS) to study the formation of MLVs in a lyotropic surfactant system (C<sub>10</sub>E<sub>3</sub>/water) using Rheo-NMR, Rheo-SALS and bulk rheology. While shear-induced transformations (using steady shear) between oriented planar lamellae and multilamellar vesicles (MLVs) have been studied in the past by Rheo-NMR [4,5], this study applied LAOS deformations in high field NMR magnets for the first time [6]. For the range of investigated strain amplitudes (10-50) and frequencies (1 rad/s, 2 rad/s) MLV formation is observed in all NMR and most SALS cases. For LAOS it was found that the MLV size mainly depends on the frequency as opposed to previous steady shear experiments where the shear rate was the controlling parameter [7]. Additionally, the onset of MLV formation using LAOS was primarily dependent on the applied shear amplitude. Furthermore, the process of onion formation appears to be retarded during LAOS as compared to the steady shear case.

[1] Diat, O. et al. Journal de Physique II, 3 1427-1452 (1993); [2] Callaghan, P.T., Rep. Prog. Phys., 62 599 (1999); [3] Samuels, J., Polym. Sci. 9, 1971, 2165; [4] Medronho, B. et. al, Soft Matter 7 4938-4947 (2011); [5] Medronho, B. et. al, Z. Phys. Chem. 226 1293-1313 (2012); [6] T.I. Brox and P. Galvosas, NZ Patent 629,361 (2016); [7] Medronho, B. et. al, Langmuir 26 1477-1481 (2010)

Wednesday 6:30 Woodway II/III

PO79

**High temperature rheometry**Denis Schuetz<sup>1</sup>, Mario Krautschick<sup>1</sup>, and Joerg Laeuger<sup>2</sup><sup>1</sup>Anton Paar GmbH, Graz, Austria; <sup>2</sup>Anton Paar Germany, Ostfildern, Germany

Rheometrical methods are well established for investigation on complex materials. An accurate temperature control is essential for correct results. However, standard heating accessories for commercial rheometers are limited to temperature of about 500°C or 600°C. Many industrial materials such as for example glass, ceramics, metals, and slags are still below their glass transition and their melting points at these temperatures. Existing devices for evaluating the rheological behavior of such materials at high temperatures are often limited to being either of a simple viscometer type or to individual designed self-made. In this paper two devices are being described which extend the temperature range for doing full rheological measurements beyond its current limit. First, a redesigned convection oven, which still fits into a standard commercial rheometer, allows measurements up to 1000°C in parallel-plate, concentric cylinder, and solid torsion geometries. With the later torsional DMTA investigations are possible. Second, a combination of a rheometer head with an external oven pushes the accessible temperature range up to more than 1700°C. In this device concentric cylinder geometries made of ceramics or platinum are used. Applications discussed in the paper range from glass, enamel, slags, aluminum alloys, basaltic melts, molten rocks, and molten salt and demonstrate the use of the described devices in performing high accurate and high precision rheological measurements at really high temperatures in many industrial and geological applications.

Wednesday 6:30 Woodway II/III

PO80

**Dripping-onto-substrate (DoS) rheometry of complex fluids**Jelena Dinic, Leidy N. Jimenez, and Vivek Sharma*Chemical Engineering, Univ of Illinois - Chicago, Chicago, IL 60607, United States*

Characterization of pinch-off dynamics and the response to both shear and extensional flows that influence drop formation/ deposition in microfluidic and printing applications requires bespoke instrumentation not available, or easily replicated, in most laboratories. Here we show that dripping-onto-substrate (DoS) rheometry protocols that involve visualization and analysis of capillary-driven thinning and pinch-off dynamics of a columnar neck formed between a nozzle and a sessile drop can be used for measuring shear viscosity, power law index, extensional viscosity, relaxation time and the most relevant processing timescale for printing. We showcase the versatility of DoS rheometry by characterizing and contrasting the pinch-off dynamics of a wide spectrum of simple and complex fluids: water, printing inks, semi-dilute polymer solutions, yield stress fluids, food materials and cosmetics. We show that DoS rheometry enables characterization of low viscosity printing inks and polymer solutions that are beyond the measurable range of commercially-available capillary break-up extensional rheometer (CaBER). We show that for high viscosity fluids, DoS rheometry can be implemented relatively inexpensively using an off-the-shelf digital camera, and for many complex fluids, similar power law scaling exponent describes both neck thinning dynamics and the shear thinning response.

Wednesday 6:30 Woodway II/III

PO81

**Newtonian versus non-Newtonian behavior of simple compressible liquids: Brillouin spectroscopy**Talgat Yakupov and Zhandos Utegulov*Physics, Nazarbayev University, Astana, Kazakhstan*

Laser-based, non-contact Brillouin light scattering spectroscopy technique was used to study viscoelastic properties of transparent aqueous glycerol solutions at GHz acoustic phonon frequencies as a function of the mass fraction of glycerol. The center frequency position of Brillouin spectral peaks is a direct measure of longitudinal storage modulus, i.e. longitudinal hypersonic sound velocity, while the linewidth of the Brillouin peak is a signature of loss modulus, i.e. total (longitudinal) viscosity of studied fluids. Measured longitudinal and shear viscosity values were used to determine bulk viscosities of glycerol-water binary mixtures by Navier-Stokes equation for viscous compressible liquids. Relaxation times for pure water, pure glycerol and mixture of the two were found from measured Brillouin spectra fitted to appropriate theoretical models for viscoelastic liquids. Shear and compressional (bulk) viscosities were also calculated from these models. The mass densities and refractive indices of studied binary mixtures were independently measured over the entire composition range at room temperature and atmospheric pressure. Since bulk viscosity of Newtonian liquids calculated by Navier-Stokes equation can only be a positive value due to the positive entropy values [1], we use this criterion to distinguish between Newtonian and non-Newtonian behavior of studied binary liquid based on critical mass fraction at which bulk viscosity changes its sign. The critical mass fraction of glycerol at which this transition takes place, was found to be ~ 60% which is in agreement with previous results measured at 20 GHz [2]. This correlates well with the rapid increase of the relaxation time, shear and compressional viscosities upon reaching this glycerol mass fraction, which is in accordance with the results reported in the literature [3, 4].

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Wednesday 6:30 Woodway II/III

PO82

**Use of a bi-fluidic, confining-fluid, pressurizable dilatometer to evaluate engineering and thermal properties of polymers and their composites**Brendan R. Ondra and Alan J. Lesser*Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States*

In a number of applications, accurate prediction of material performance requires a more thorough characterization of the material's engineering properties. In many cases, measurements of the in-plane properties are insufficient to fully evaluate all the properties necessary to predict the elastic, viscoelastic, and thermoelastic constitutive response. In this work, we use a new pressurizable dilatometer to measure bulk properties of both isotropic and anisotropic media. We will demonstrate its use in the evaluation of pressure and temperature dependent transitions as well as the bulk thermoelastic response between these transitions. We will then illustrate how these types of measurements can be done on anisotropic media (carbon fiber reinforced composites and polymer films) to evaluate their out-of-plane constitutive response when these measurements are coupled with complimentary in-plane measurements. We also detail a new bi-fluidic confining-fluid pressurizable dilatometer that was used to conduct this work. Whereas the majority of classical confining-fluid dilatometers make use of a bellows, our design concept centered around replacing the bellows with a fluid-fluid interface composed of two immiscible liquids that have different densities. This design change enables us to overcome the mechanical and operational restrictions that are inherent to the use of a bellows. For the hydraulic fluid, we selected an ionic liquid (1-ethyl-3-methylimidazolium ethyl sulfate) because ionic liquids have been shown to possess bulk properties which are superior to traditional hydraulic fluids. For the confining fluid, we selected a liquid metal, Galinstan. This liquid metal possesses the appropriate thermal and mechanical properties for this application. The temperature and pressure ranges for our dilatometer span 25C-250C and 7MPa-186MPa, respectively, and over these ranges, the rates of heating, cooling, and pressurization are well controlled. With a sample size of up to 2mL, we can detect volume changes down to 1µL.

Wednesday 6:30 Woodway II/III

PO83

**Using digital image correlation to monitor the localized degradation of polyethylene exposed to weathering**Aaron R. Forest<sup>1</sup>, Donald Hunston<sup>2</sup>, Jae-Hyun Kim<sup>3</sup>, and Christopher C. White<sup>2</sup><sup>1</sup>Winston Churchill High School, Rockville, MD 20852, United States; <sup>2</sup>Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States; <sup>3</sup>NIST, Gaithersburg, MD 20899, United States

This poster will detail the use of Digital Image Correlation (DIC) technique to monitor the direct strain of polyethylene as a function of environmental exposure. Previous studies have suggested a mechanism for the degradation of polyethylene, (specially Dow 2480, HDPE) that involves chain scission that produces an increase in surface crystallization. This surface crystallization is proposed to decrease in the mechanical properties of the polyethylene, specifically the elongation to break changes from ~700% to <10%. The DIC technique allows for direct observation of the strain distribution during mechanical testing. If the independently measured increase in crystallization with environmental exposure is impacting the mechanical properties then the DIC should show the actual distribution of the strain in the sample during testing. If surface crystallization increases during weathering, then a concentration of the local strain should be evident in the DIC analysis.

Wednesday 6:30 Woodway II/III

PO84

**Replacement of the manual torsion tester with a rotational rheometer for the determination of the Clash-Berg flex temperature of plastics**Gregory W. Kamykowski*TA Instruments, Wood Dale, IL 60191, United States*

An important thermo-mechanical property of plastics is the Clash-Berg flex temperature (Tf). This is defined as the temperature at which the material has an apparent modulus of 310 MPa at 5 seconds after the imposition of a stress that is in the linear viscoelastic region. This is described in ASTM D1043. The instrument that has been used for this test is a manual torsion tester which does not give a permanent record of the test, and it uses a time-consuming fluid bath to control temperature. Furthermore, this instrument is no longer manufactured in the United States. It would be beneficial to convert this test to a modern rheometer that does give one an actual data file and controls the temperature with an efficient oven, rather than a fluid bath. PVC samples that ranged in Tf from -64 C to +6 C were evaluated on rotational rheometers, and the results were compared with data from the manual torsion tester. The agreement between the Tf values obtained with the two devices was excellent. A recommendation will be made to include rheometer testing in ASTM D1043 when this method gets revised.

Wednesday 6:30 Woodway II/III

PO85

**Using large amplitude oscillatory shear (LAOS) method to quantify polymer long chain branching**Tianhong T. Chen<sup>1</sup> and Gregory W. Kamykowski<sup>2</sup><sup>1</sup>Applications, TA Instruments - Waters LLC, New Castle, DE 19720, United States; <sup>2</sup>TA Instruments, Wood Dale, IL 60191, United States

Branching in polymers contributes many unique rheological properties in polymer processing. Polymer branching enhances chain entanglements, increases relaxation times, and increases the extensional flow viscosity as evidenced by the strain hardening phenomenon. For many years, researchers have used different rheological methods attempting to quantify the degree of branching in polymer chains. The most commonly used rheological techniques for differentiating linear versus long chain branched polymers include melt frequency sweeps followed by time-temperature superposition (TTS), and extensional viscosity testing. In recent years, large amplitude oscillatory shear testing (LAOS) has provided a new and more sensitive approach for analyzing branching structures. However, due to the elastic characteristic of the polymers, LAOS tests conducted using general parallel plate or cone and plate geometries are challenging due to edge fracture. The RPA rheometer uses a bi-cone geometry with a closed die design. It successfully prevents edge fracture from occurring at large strain amplitudes. In this paper, we discuss using the LAOS method on an RPA rheometer to quantify the degree of long chain branching. A series of high molecular weight HDPE polymers with very small amount long chain branching structures were tested. Traditional size exclusion chromatography (SEC) method cannot differentiate the amount of branching of these resins. Neither were dynamic frequency sweeps on the molten materials. It is observed that the LAOS higher harmonic signals G3' and G5' are sensitive to branching structures. The long chain branching index was quantitatively calculated based on an empirical equation.

Wednesday 6:30 Woodway II/III

PO86

**Dynamic oscillatory testing and viscoelastic characterization of aqueous fluids under pressure**Alina K. Latshaw*TA Instruments, New Castle, DE 19720, United States*

Characterizing viscoelastic properties of fluids at temperatures above boiling poses significant challenges, most notably the boiling of volatile ingredients resulting in changes to material composition. Various methods and apparatuses have been employed to trap solvents or suppress evaporation; these slow compositional changes at higher temperatures but are ineffective beyond the boiling point. A pressurized testing environment is the only means to characterize the rheological properties of materials under such conditions. Many commercialized rheometer pressure cells are inherently limited in torque sensitivity due to the reliance on mechanical bearings. These limit the measurable range of shear stresses and viscosities, and confine testing to steady shear protocols. Naturally, this precludes the measurement of important viscoelastic properties and alters structured fluids such as gels and suspensions, where steady shear suppresses the modulus of the fully formed structure and does not accurately represent the quiescent state properties. In this poster, we demonstrate the viscoelastic characterization of aqueous solutions through dynamic oscillatory testing using a novel flow cell that provides atmospheric pressure and temperature control in a controlled-strain shear

reometer. The absence of a mechanical bearing provides the low torque sensitivity required for dynamic testing. Evidence of functionality will be demonstrated using gelling solutions, dilute polymer solutions, and various suspensions and emulsions.

Wednesday 6:30 Woodway II/III

PO87

### **Remote and in-line sensing of viscosity by EMS system**

Keiji Sakai<sup>1</sup>, Taichi Hirano<sup>1</sup>, Yoshikazu Yamakawa<sup>2</sup>, and Maiko Hosoda<sup>3</sup>

<sup>1</sup>Fundamental Engineering, Inst Indust Sci, UTokyo, Meguro-ku, Tokyo 153-8505, Japan; <sup>2</sup>Triple Eye Co. Ltd., Kyoto, Japan;

<sup>3</sup>Tokyo Denki University, Saitama, Japan

Among various kinds of rheology measurement apparatus, the Electro-Magnetically Spinning (EMS) system has a remarkable feature, that is the remote induction of the driving torque to the rotating viscosity probe immersed in fluid samples. A probe is made of conducting metal and the rotating magnets placed around or below the probe induces temporally modulating magnetic field to the probe. Current is then induced in the metal probe and then, the Lorentz interaction between the excited current and the applied magnetic field gives a torque to the probe so that it follows the rotation of the magnetic field. The probe is immersed in the sample and it rotates feeling the viscosity of the surrounding medium. The value of the viscosity is then given from the relation between the rotational speeds of the magnetic field and the probe. The EMS system can drive the probe in a non-contact manner, and therefore, it would be used for the remote sensing of the viscoelastic properties in, for example, reactors, reserves and pipe-lines. In this study, we examined the possibility of application of the EMS system to the in-line measurement of rheology. For the demonstration of the remote sensing of viscosity with the distance larger than 30 mm, we measured the shear viscosity of the pure water in the cooling process. The initial temperature of water was 80 C and was poured into an insulation paper cup. The rotation of the probe is observed by a video camera and the viscosity is obtained from the rotational speed determined though the image analysis. As a result, we could measure the change of the viscosity in cooling process with the accuracy of 2%. In conclusion, a fundamental examination to apply the EMS system to the remote sensing of the rheological properties was carried out. In the presentation, we would propose further result to detect the change of the rheological properties accompanying the proceeding chemical reaction.

Wednesday 6:30 Woodway II/III

PO88

### **A rheo-DMA platform for extended polymer analysis**

Abhishek Shetty<sup>1</sup>, Alexander Troiss<sup>2</sup>, and Gunther Arnold<sup>3</sup>

<sup>1</sup>Rheology, Anton Paar USA, Ashland, VA, United States; <sup>2</sup>Rheology, Anton Paar GmbH, Graz, Austria; <sup>3</sup>Rheology, Anton Paar

Germany, Ostfildern, Germany

A new measuring device concept is introduced which combines an electronically commutated (EC) motor as rotational top drive and a moving magnet linear drive or another EC motor, as bottom drive to enable rheological measurements and dynamic mechanical analysis (DMA) on one single device. The concept enables various modes of operation by using different combinations of the bottom drive. Besides working in the rheological modes such as separate motor transducer (SMT), combined motor transducer (CMT), counter-rotation and counter-oscillation the device is suitable to perform dynamic mechanical analysis in bending, tension, compression, and torsion as well as thermomechanical analysis (TMA). In this study different examples are used to describe the different demands of polymer testing and the broad spectrum of operation modes necessary for a comprehensive characterization of polymers. The example of the dynamic mechanical analysis of a fiber reinforced polymer (FRP) is used to indicate the impact of the fiber direction on the mechanical behavior of the specimen which is mainly affected by different matrix-fiber interactions. In a further example the characterization of a 3D printed polyether ether ketone (PEEK) highlights the impact of the printing orientation on the dynamic mechanical properties of the material. Additionally, the investigation of the shape memory effect of a thermoplastic polyurethane (TPU), the thermomechanical behavior of a FRP and various rheological measurements are used to demonstrate the flexibility and versatility of such a flexible device for extended polymer characterization and to outline further applications for the characterization of anisotropic materials.

Wednesday 6:30 Woodway II/III

PO89

### **Rheology as a tool for understanding thermoset coating cure and property development**

Steven V. Barancyk, Hao Sun, and Francesca A. Johnson

Coatings Innovation Center, PPG, Allison Park, PA 15101, United States

Cure of a thermoset coating is a complex process involving solvent evaporation, flow and levelling of the component resins, and ultimately crosslinking via chemical reactions. It is influenced by coating factors such as solvent evaporation rate, binder resin characteristics (e.g. Tg, structure, and molecular weight), rheology control additives, pigmentation, and catalysts, and process factors such as temperature and bake time. By monitoring the rheological behavior of a coating under conditions that mimic the conditions it experiences during the application and bake process, insight can be gained into the development of coating appearance and physical properties.

Wednesday 6:30 Woodway II/III

PO90

### **Evaluating temperature dependence of local mechanical property by temperature variable AFM**

Yuichi Kasai

Hitachi High-Technologies Science America, Inc., Chatsworth, CA 91311, United States

We developed a new scanning method that a cantilever can move vertically and a sample stage which is more improved the range of temperature variable. Temperature dependence of local mechanical property of blended rubber at nano area was investigated by using temperature variable

Scanning Probe Microscope; SPM. The blended rubber which includes natural rubber; NR, and butadiene rubber; BR, was deformed by the cantilever and the Young modulus was calculated from slope of load-displacement curves obtained at every pixel. The image contrast showing the distribution for Young's modulus at -90 °C was clearly observed according to difference of BR in rubbery region and NR in glassy region. At 25 °C where both components, BR and NR, are in rubbery region, the image contrast of Young's modulus disappeared. Also, as a results of adapting several contact models, Young's modulus obtained from these models approximated to Young's modulus measured by DMA.

Wednesday 6:30 Woodway II/III

PO91

### **Interfacial exchange cell: New possibilities for subphase modification in interfacial rheology**

Kevin J. Whitcomb, Bharath Rajaram, and Aloyse Franck

*Applications, TA Instruments, New Castle, DE 19720, United States*

Characterizing the viscoelastic properties of interfaces is critical to understanding and controlling the formulation of biotherapeutics, emulsions used in food and personal care products, and increasing yields in enhanced oil recovery techniques. Surface tension has traditionally been used to study interfacial properties through geometries like the Wilhemy plate, du Nouy ring, and Langmuir trough. More recently, the development of the patented Double Wall Ring (DWR)<sup>1</sup> geometry has permitted the characterization of weak viscoelastic interfaces on commercial rheometers. While these techniques allow the study of multi-phase systems, the composition of the individual phases is kept constant throughout the test. In this study, we extend the capabilities of the DWR geometry with a new Interfacial Exchange Cell that enables the ability to manipulate the chemistry of the subphase during rheological measurements. The cell design, based on computational fluid modeling by Schroyen et al.<sup>2</sup>, employs a series of fluid inlet and outlet ports to infuse a new subphase during the experiment. These ports are strategically placed to facilitate maximum mixing while minimizing interfacial stress and maintaining a constant fluid height. The study presents results from a series of tests using the subphase exchange cell installed on a TA Instruments Discovery Series HR-3 rheometer. Specifically, a stable Bovine Serum Albumin protein interface is used to explore the effects of subphase protein concentration and the impact of introducing surfactants into the subphase. The broader implications of this unique ability to manipulate the subphase chemistry for drug delivery, biofilm growth, personal care and food products are discussed.

<sup>1</sup> US Patent #: 7,926,326; <sup>2</sup> Schroyen, B.; Gunes, D.Z.; Vermant, J. *Rheologica Acta* **2017**, 56, p1-10

Wednesday 6:30 Woodway II/III

PO92

### **Small volume capillary rheometry**

Steven Hudson<sup>1</sup>, Paul F. Salipante<sup>1</sup>, David Yoon<sup>1</sup>, Ryan P. Murphy<sup>2</sup>, and Katie M. Weigandt<sup>2</sup>

<sup>1</sup>*Polymers and Complex Fluids Group, National Institute of Standards and Technology, Gaithersburg, MD 20910, United States;*

<sup>2</sup>*Center for Neutron Research, NIST, Gaithersburg, MD 20899, United States*

Small sample test volumes are convenient, in some applications essential. We use various custom capillary rheometers to achieve small volumes (microliters), high shear rate, and wide dynamic range of shear rate and viscosity. Methods and results will be described. Scattering and microscopy of the sample are also included.

Wednesday 6:30 Woodway II/III

PO93

### **Combined rheo-Raman analysis: Correlating viscoelastic behavior with chemical structure**

Bharath Rajaram<sup>1</sup> and Jennifer Ramirez<sup>2</sup>

<sup>1</sup>*TA Instruments, New Castle, DE, United States;* <sup>2</sup>*Thermo Fisher Scientific, Madison, WI, United States*

Rheology offers powerful methods for studying a material's response to shear deformation and changes in environmental conditions. In addition to bulk rheology measurements, there is often a strong desire to explore the relationship between the sample microstructure, chemistry, and the observed mechanical response. Of these, structure visualization through microscopy and scattering techniques is well established in literature. In this study, we present a new rheo-Raman setup that permits chemical structure characterization during rheological measurements. Raman spectroscopy provides critical information about molecular structure and bonding and can elucidate intermolecular interactions of pure components and mixtures. Details are provided for a turnkey system that integrates a commercially available rheometer (Discovery Series HR-3, TA Instruments) with a Raman spectrometer (iXR, Thermo Fisher Scientific). The setup offers temperature control and ensures Class I laser safety through appropriate safety interlocks. Results are presented for the crystallization of a pure polyethylene glycol (PEG) melt studied by Differential Scanning Calorimetry (DSC) and simultaneous rheo-Raman spectroscopy. As the temperature is decreased, the polymer's liquid-to-solid transition is marked by a significant increase in the moduli. Simultaneous collection of Raman spectra indicate an increase in molecular interactions and order that coincides with changes in bulk rheology. Additional examples of rheo-Raman spectroscopy are presented for commercial materials. In one case of a commercial cosmetic lotion, the temperature dependent decrease in viscosity directly correlates with changes in the C-C and C-H stretching modes that are sensitive to conformational disorder. The results highlight the importance of hyphenated rheometric techniques to fully understand the origins of material viscoelasticity.

Wednesday 6:30 Woodway II/III

PO94

**New, practical rheological tools for QA/QC monitoring of gelation or cure**David J. Moonay*AMETEK Brookfield, Middleboro, MA 02346, United States*

Thermoset materials are important and widely used in numerous industries and applications. This paper discusses new instruments and accessories developed for monitoring gelation or cure. The equipment development was performed at the request of thermoset resin manufacturers, to fill a void left by a popular system that was discontinued. Firmware modifications were performed on compact, bench-top, laboratory viscometers and rheometers, allowing a standard testing protocol to be performed. The apparatus can measure the gel time and the peak exotherm temperature, as well. A new, quick-attachment union was created, to hold the consumable rod immersed in the sample. The equipment is described and results are presented, herein.

Wednesday 6:30 Woodway II/III

PO95

**End effect correction for orthogonal superposition of small strain oscillatory shear in a rotational shear rheometer**Ran Tao and Aaron M. Forster*Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

The orthogonal superposition (OSP) technique, first introduced by Philippoff in 1934, involves superimposing a small amplitude oscillation orthogonal to a primary shear flow. This technique allows for probing micro-structural changes in complex fluids under nonlinear flow conditions, as the flow in the axial and angular directions are not coupled. The OSP functionality has been implemented in a commercial ARES-G2 rheometer utilizing a double wall concentric cylinder geometry. The fluid is sheared by rotation of the inner and outer cylinders (cup), while an axial oscillation is applied to the center cylinder (bob) simultaneously. The design of the flow cell is optimized for a more homogeneous flow field by adding windows to the bottom of the inner cylinder and top of the bob. The bottom windows minimize fluid pumping and the top windows eliminate surface tension effects. During the OSP operation, the nominal shearing surface is the distance between the top and the bottom windows. Experimental error can arise from drag flow between these surfaces and boundary forces at the leading edges of the bob as it pushes through the fluid. An empirical orthogonal end-effect factor is implemented in the geometry constant to compensate this boundary effect in the instrument settings. The value of the orthogonal end-effect factor is determined by shifting the orthogonal complex viscosity to agree with the primary shear viscosity. The current work focuses on end-effect factor calibration measurements using different viscosity standards that range from 0.01 to 100 Pa.s. The end-effect factor was found to depend on fluid properties and oscillation rates. Understanding the correction due to non-idealized flow field in the confined geometry is particularly important for the study of complex fluid systems where viscosity may vary by a few orders of magnitude across a narrow strain rate range. The results from the study should inform other OSP users with better operational knowledge to calibrate the instrument.

Wednesday 6:30 Woodway II/III

PO96

**Random-frequency sweeps: Empirical examples**Montgomery T. Shaw*Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, United States*

For systems where time is a factor, a random-frequency sweep can be used to extract the frequency information by incorporating time effects into the random error. In a previous presentation [1], the results of illustrative numerical examples were discussed, showing that a random-frequency sweep can uncover the fixed-time frequency dependence quite well. The purpose of this work is to compare experimental findings using a random-frequency sweep with the time-consuming process of running time sweeps at constant frequencies. A chosen time effect was the loss of a small amount of toluene from a silicone gum. Also attempted was a curing system using a gelatin solution cooled to 10 °C. As with all systems showing time effects, a principal experimental issue is establishing a repeatable zero-time condition.

[1] Shaw, M. T., 89th Annual Meeting of the Society of Rheology, 2017, Abstract PO36, p. 99.

Wednesday 6:30 Woodway II/III

PO97

**Impact of instrument inertia on oscillatory shear measurements with rotational rheometers**Gunther Arnold, Heiko Stettin, Joerg Laeuger, and Tobias Nill*Anton Paar Germany, Ostfildern, Germany*

There are two different operating principles for rotational rheometers. In one design, the torque is measured at the moving surface, i.e. the motor current is taken as a measure of the torque. The working mode of such rheometers is called combined motor transducer (CMT) mode. Historically, such types of rheometers are also known as stress controlled instruments. In a different design, a motor drives one member of the geometry and the torque is measured as the torque, which is needed to keep the second member nearly fixed. This working mode is called separate motor transducer (SMT) mode and historically such types of rheometers are called strain controlled instruments. Because in a CMT mode the torque is measured at the moving surface, the moment of inertia of the moving parts of the instrument might influence the measurement results. Therefore responsible is a large ratio of acceleration to sample torque which is a function of the momentum of inertia of the measuring system, the angular frequency, the modulus of the complex viscosity and the geometry factor (k) of the measuring system. The geometry factor k is inversely

proportional to the radius to the third power (cone-and-plate) or fourth power (plate-plate). Hence, increasing the radius of the measuring system can reduce the ratio of acceleration to sample torque and increase the accuracy of the determination of rheological properties. Contrary to this, in SMT mode instrument inertia effects can be neglected. In order to investigate inertia effects oscillatory shear measurements have been performed with different measuring geometries using a MCR 702 rheometer suitable to work in CMT and SMT mode. For a CMT situation, it is shown that with an appropriate control mechanism, taking into account the instrument inertia, reliable results can be achieved and measurements up to relatively large frequencies are possible.

Wednesday 6:30 Woodway II/III

PO98

### Testing the paradigm of an ideal glass transition by measuring viscoelastic properties of ultrastable polymeric glass

Gregory B. McKenna and Heedong Yoon

*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

The dynamic behavior of glass forming liquids remains one of the greatest challenging problems in condensed matter physics. [1, 2] One important question is whether the equilibrium dynamic response deep in the glassy state follows super-Arrhenius behavior. [2] However, accessing the equilibrium dynamics deep in the glassy state requires geological aging times for the measurements, hence it is virtually impossible to investigate the equilibrium dynamics by simply aging sample for millions of years. [3] Recently, we have developed a vapor deposition approach to create ultrastable amorphous Teflon films [4] having a 57 K fictive temperature ( $T_f$ ) reduction relative to the glass transition temperature ( $T_g$ ). This large  $T_f$  reduction is close to the Kauzmann temperature, and gives an opportunity to study the dynamic behavior deep in the glassy regime. Here, we use this ultra-stable glass to study the relaxation behavior of the polymer in the temperature range between  $T_f$  and  $T_g$  where the glass has longer relaxation time than the equilibrium system. The relaxation behavior of stable Teflon films was measured using the TTU nano bubble inflation technique [5] by following Struik's protocol [6]. We found that there is a strong deviation from VFT dynamics in the upper bound regime suggesting that the ideal glass transition may not exist.

[1] Anderson, P. W. *Science* 1995, 267, 1615. [2] McKenna, G. B.; Simon, S. L. *Macromolecules* 2017, 50, (17), 6333-6361. [3] Zhao, J.; Simon, S. L.; McKenna, G. B. *Nat. Commun.* 2013, 4, 1783. [4] Yoon, H.; Koh, Y.P.; Simon, S.L.; McKenna, G. B. *Macromolecules*, 2017, 50, 4562-4574. [5] O'Connell, P. A.; McKenna, G. B. *Rev. Sci. Instrum.* 2007, 78, 013901-1-013901-12. [6] Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978.

Wednesday 6:30 Woodway II/III

PO99

### Decoupling polymeric and colloidal contributions to the rheology of self-suspended grafted nanoparticle melts

Daniele Parisi<sup>1</sup>, Ellie Buenning<sup>2</sup>, Brian Benicewicz<sup>3</sup>, Sanat Kumar<sup>4</sup>, and Dimitris Vlassopoulos<sup>1</sup>

<sup>1</sup>*Materials Science and Technology-University of Crete, FORTH-IESL, HERAKLION, Greece;* <sup>2</sup>*Columbia University, New York, NY, United States;* <sup>3</sup>*University of South Carolina, Columbia, SC, United States;* <sup>4</sup>*Columbia University, New York, NY, United States*

Using a series of well-characterized polymer-grafted silica nanoparticles with the same hard core size and grafting density, we investigate their linear viscoelastic response in the melt state as function of increasing molar mass of the grafted chains, i.e., with decreasing core volume fraction. We identify two modes of relaxation, a faster one associated with the grafted chains and a slower one reflecting the overall nanoparticle hopping. These modes are quantified by means of tube and mode coupling theory modeling, respectively, by accounting for the molecular features of the particles and the estimated stretched inner part of the grafted layer, where interpenetration with chains from other nanoparticles is virtually impossible. Consequently, the two modes can be decoupled and, importantly, the transition from polymer- to colloid-dominated response is identified. Further, we discuss the respective signatures in nonlinear shear and focus on the yielding process in an attempt to provide material parameters for tailoring the response of such soft composites.

Wednesday 6:30 Woodway II/III

PO100

### Mechanical and electrical properties of poly(ethylene oxide)/carbon nanotube nanocomposites

Nirosh Getangama, John R. de Bruyn, and Jeffrey L. Hutter

*Physics and Astronomy, University of Western Ontario, London, Ontario N6A 3K7, Canada*

We study the mechanical and dielectric properties of poly(ethylene oxide)/multiwalled carbon nanotubes (PEO/MWCNT) composites made by melt mixing and compression molding. Small-amplitude oscillatory shear measurements were performed as a function of MWCNT concentration  $c$  and temperature  $T$  close to and above the melting temperature of PEO. Dielectric properties were studied for frequencies from 1 mHz to 1 MHz as a function of  $T$  and  $c$  using a dielectric spectrometer. Both the elastic and viscous moduli of the composite increased with increasing MWCNT concentration. At low  $c$  and temperatures above the melting temperature, the moduli show Maxwell-like behavior, with a crossover corresponding to a characteristic relaxation time. Increasing  $c$  causes the mechanical relaxation time of the nanocomposites to increase, and at high concentrations, the elastic modulus dominates at all frequencies. The dielectric relaxation time and DC conductivity were extracted from the dielectric spectra using existing models. Our data for PEO/MWCNT show that an electrical percolation transition occurs for  $c$  between 1 and 1.5 wt%. Both dielectric and mechanical data show that polymer relaxation is altered by the interaction between the nanotubes and PEO polymer chains.



Wednesday 6:30 Woodway II/III

PO101

**Effect of surface geometry on the frictional properties of poly(dimethyl siloxane)**Yunhu Peng, Christopher M. Serfass, and Lilian C. Hsiao*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States*

Natural cartilage is durable and elastic, providing a low friction coefficient to moving joints under frequent applications of heavy loads. However, the physical mechanisms contributing to this low friction coefficient is not well understood. We hypothesize that the non-ideal surface geometry of cartilage gives rise to its low friction coefficient in certain directions of motion. We design microtextured soft poly(dimethyl siloxane) (PDMS) substrates with lithography to study the influence of surface geometry on their frictional and lubrication properties. The PDMS surfaces consist of stripes with controlled dimensions and spacings between each other. Tribological tests performed with a thin layer of aqueous glycerol solution at different concentrations between the PDMS substrates show that the friction coefficient is a function of the sliding velocity. However, this tribological behavior does not follow the type of Stribeck curve that is typically observed with flat surfaces. Two major differences are observed at different velocity ranges. First, a significant frictional reduction is observed in the boundary regime where the sliding speed is relatively low. Second, a velocity-dependent friction peak is observed in the elastohydrodynamic lubrication (EHL) regime. We hypothesize that this friction peak arises due to the competition between micro-EHL and EHL at the microtextured surfaces. To test this hypothesis, we develop scaling theories that show how the localized maximum friction is a function of the differential lubrication generated by the geometry of the microtextured surfaces.

Wednesday 6:30 Woodway II/III

PO102

**Fatigue analysis via Fourier transform of the stress**Valerian Hirschberg<sup>1</sup>, Manfred Wilhelm<sup>2</sup>, and Denis Rodrigue<sup>1</sup>*<sup>1</sup>Department of Chemical Engineering and CERMA, Université Laval, Quebec City, Quebec G1V 0A6, Canada; <sup>2</sup>Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Karlsruhe 76128, Germany*

In this work, the stress response of mechanical testing on notched rectangular solid polystyrene (PS), polymethylmethacrylate (PMMA) and styrene-acrylonitrile (SAN) samples in oscillatory shear was analyzed via Fourier transform (FT) to determine fingerprints of continuous fatigue. The tests were performed at room temperature using a torsion geometry and were filmed to visualize changes. Large strain amplitudes were applied so the stress response was nonlinear and higher harmonics were detected via FT. The idea is to analyze the time evolution of the stress via linear (storage ( $G'$ ) and loss ( $G''$ ) moduli) and nonlinear parameters (higher harmonics), their derivatives and integrals. These parameters were used to better understand fatigue, to detect and describe specific events such as crack initiation and propagation, to predict the fatigue lifetime and to develop failure criteria. The linear parameters ( $G'$ ,  $G''$ ) were found to decrease monotonically, while the  $I_{3/1}$  intensity (relative amplitude of the third harmonic to the fundamental one) steadily increased until failure. These three parameters were found to change linearly with the cycle number, shortly after the beginning of the test until failure onset. The fatigue lifetime was found to follow a power-law function of the rates of change of  $G'$ ,  $G''$  and  $I_{3/1}$  in this regime. For undamaged samples, the nonlinear parameter  $I_{2/1}$  is within the noise level, but its intensity increased when macroscopic cracks were created. Additionally, to better understand the origin of failure, the integral of the nonlinearity ( $Q = I_{3/1}/\omega^2$ ) until failure was analyzed as a function of the fatigue lifetime. A power-law function between the integral of  $Q$  and the fatigue lifetime was found. The time evolution of  $G'$ ,  $G''$ ,  $I_{3/1}$ ,  $I_{2/1}$  and the integral of  $Q$  as a function of the fatigue lifetime, are proposed as new, highly sensitive, criteria to predict failure and detect the onset of macroscopic cracks.

Wednesday 6:30 Woodway II/III

PO103

**Tribological properties of hard and soft surfaces with grafted polyzwitterionic brushes**Christopher M. Serfass and Lilian C. Hsiao*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States*

Recent studies show that biomimetic surfaces with grafted polyzwitterionic brushes can attain extremely low friction coefficients and increased wear resistance. These types of engineered surfaces are increasingly important in applications such as self-cleaning and anti-fouling coatings. Our goal is to investigate the steady state and transient tribological response of hard and soft surfaces as a function of the interfacial dynamics of grafted polyzwitterionic brushes. Here, we employ atom transfer radical polymerization (ATRP) to grow polymer brushes from hard silicon wafers ( $E \sim 10^{11}$  Pa) and soft poly(dimethyl siloxane) substrates ( $E \sim 10^6$  Pa). This grafting-from process grows monomers one unit at a time from initiators attached a priori onto the surfaces. The polymer brushes are then betainized to produce polyzwitterionic brushes. We characterize polymer brush layers using spectroscopic ellipsometry to determine brush thickness, and Fourier-transform infrared spectroscopy (FTIR) to confirm the presence of appropriate functional groups. Separately, we perform tribological characterization of the native and polymer-grafted surfaces using a ball-on-3-plates geometry attached to a stress-controlled rheometer, in which the surfaces are fully immersed in a liquid medium. We find that betainization changes the friction coefficient of polymer brushes, but fails to produce friction coefficients lower than those of untreated silicon. To address this issue, we will investigate the pre-ATRP chemical modifications and their effects on the surface energy of the substrates.

Wednesday 6:30 Woodway II/III

PO104

**Dynamics of polymer-grafted nanoparticles controlled by soft confinement**Ali Slim, Ryan Poling-Skutvik, Jacinta C. Conrad, and Ramanan Krishnamoorti*Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United States*

Polymer-grafted nanoparticles (PGNPs) can enhance the properties of composites and improve the biocompatibility of targeted drug delivery. Improved understanding of the structure and dynamics of these materials is key to advancing their performance in applications. There are three

size regimes of interest when studying PGNPs. When the radius of gyration  $R_g$  of grafted polymer is much smaller than NP radius  $R_{NP}$ , dynamics of PGNPs are expected to be similar to those of hard spheres. Conversely, when  $R_g$  is much larger than  $R_{NP}$ , PGNPs behave like dendritic or star polymers. In the intermediate regime where  $R_g$  and  $R_{NP}$  are comparable, the structure and dynamics become influenced by both the hard (NP-NP) and soft (polymer-polymer) interactions. This regime is not well understood.

Using a “grafting-to” procedure, we graft high molecular weight polystyrene ( $M_w = 355$  kDa,  $R_g = 21$  nm) on spherical silica nanoparticles ( $R_{NP} = 24$  nm) and disperse these PGNPs in solutions of free linear polystyrene of molecular weight 150, 590, and 1100 kDa in 2-butanone. We characterize the structure and dynamics of this system using neutron and x-ray scattering, respectively. The grafted polymer chains are compressed in the presence of free polystyrene due to an increase in osmotic pressure of the solutions. The dynamics of PGNPs decouple from bulk viscosity and deviate from the behavior predicted for hard spheres. These results suggest that the grafted polymer introduces soft interactions between the nanoparticles and free polymers that generate deviations from the expected behavior.

Wednesday 6:30 Woodway II/III

PO105

### **Nano-rheological measurements of ultrathin amorphous fluoropolymer films**

Amer A. El Banna and Gregory B. McKenna

*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409-4121, United States*

We use vacuum pyrolysis deposition to produce thin ultra-stable Teflon films. We compare confinement effects and viscoelastic properties of ultra-stable films with their rejuvenated films. The viscoelastic response of freely standing Teflon films were characterized using the novel bubble inflation technique [P. A. O'Connell and G. B. McKenna, *Science* 307, 1760-1763 (2005)] on films ranging from 30 - 275 nm and over a temperature range of  $T_g(\text{macroscopic})-15^\circ$  to  $T_g(\text{macroscopic})+20^\circ$ . Imaging capabilities of the atomic force microscope were used to capture the bubble geometry's time evolution. Time-temperature superposition, time-thickness superposition and rubbery stiffening are to be discussed.

Wednesday 6:30 Woodway II/III

PO106

### **Characterization of clay-based magneto-rheological composite materials for structural applications**

Travis L. Thornell, Sarah L. Williams, Zackery B. McClelland, and Todd S. Rushing

*US Army Engineer Research and Development Center, Vicksburg, MS 39180, United States*

Magneto-rheological composite materials have the potential to allow for instant and adaptable control of structural components. The ability to create temporary structures from soft materials by applying a stimulus such as a magnetic field enables for storage and transportation that would not be feasible otherwise. This study investigated a model system of non-magnetic clay slurry embedded with magnetic iron particles to understand how slurries behave in applied magnetic fields. Characterization of various iron-based particles using vibrating sample magnetometry (VSM), scanning electron microscopy (SEM), and particle size analysis were used to determine magnetic properties and particle characteristics and to select the best candidates for rheological characterization. From VSM results, carbonyl iron particles (CIP) were selected based on having a high magnetic field strength and ability for future scalability. Slurries composed of kaolinite and CIP dispersed in mineral oil were formulated. Initial slurry compositions varied from high solids content forming thick slurries to low solids loading with lower viscosities. Rheological characterization was performed using a parallel plate geometry with attached magneto-rheology accessory to apply magnetic flux densities up to 1 Tesla during the experiments. Magnetic time sweeps were conducted on the slurries to observe storage modulus changes as a function of increasing magnetic field that indicated assembly of the CIP stiffening the slurries. Oscillatory tests were implemented to determine the viscoelasticity of the slurries based on the applied magnetic field environment. The rotational behavior was studied using flow curves and constant applied shear experiments to determine changes in viscosity and influence of particle assembly and jamming.

Wednesday 6:30 Woodway II/III

PO107

### **Mechanical hole-burning spectroscopy of polymer glasses**

Satish Chandra Hari Mangalala and Gregory B. McKenna

*Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Non-linear mechanics of soft materials like polymer melts or polymer solutions are frequently investigated by Large Amplitude Oscillatory Shear spectroscopy (LAOS) tests. Less work has been reported on the characterization of the non-linear viscoelastic properties of glassy polymers within a similar framework. In the present work we are using an extension of LAOS, i.e., mechanical spectral hole burning (MSHB) to investigate the nonlinear dynamics of polymers in the deep glassy state. MSHB has been developed as an analog to non-resonant spectral hole burning (NSHB) developed by Schiener et al. who attributed the presence of holes to dynamic heterogeneity. On other hand McKenna (and co-workers) in their works on polymer solution and melts, attributed the presence of holes to the type of dynamics rather than to a specific spatial heterogeneity. In MSHB, a small probe response is investigated after a large sinusoidal pump deformation. A series of three experiments are performed to investigate the presence of holes. In the first experiment, the sinusoidal pump is applied followed by a small positive probe deformation. In the second, the pump is followed by a negative probe deformation. The difference in these two probe responses divided by 2 gives a “modified response”. This modified response is compared with the simple “linear response” from a third experiment. The differences between these two responses can lead to the formation of holes. Similar experiments are being performed on polycarbonate and poly(methyl methacrylate) in the glassy state to investigate the presence and origin of holes, if any, and how they relate to the differences in the strengths of the  $\beta$ -relaxation in the two polymers.

Wednesday 6:30 Woodway II/III

PO108

**Interplay of deformability and adhesion on margination of elastic micro-particles in blood flow**Ying Li*Department of Mechanical Engineering, The University of Conn, University of Connecticut, Storrs, CT 06269, United States*

We numerically study the margination behavior of elastic MPs to blood vessel wall under the interplay of their deformability and adhesion to vessel wall. Margination probability is used to quantify the margination propensity of elastic MPs. Two dimensionless numbers are considered to govern the whole process: the capillary number  $Ca$ , denoting the ratio of viscous force of fluid flow to elastic interfacial force of MP, and the adhesion number  $Ad$ , representing the ratio of adhesion strength to viscous force of fluid flow. We systematically vary them numerically and a margination probability contour is obtained. We find that there exist two optimal regimes favoring high margination probability on the plane  $Ca$ - $Ad$ . The first regime, namely region I, is that with high adhesion strength and moderate particle stiffness, and the other one, region II, has moderate adhesion strength and large particle stiffness. We conclude that the existence of optimal regimes is governed by the interplay of particle deformability and adhesion strength. The corresponding underlying mechanism is also discussed in detail. There are three major factors to contribute to the margination behavior of MPs: (i) hydrodynamic collision between RBCs and MPs; (ii) deformation induced lift force due to the presence of wall; (iii) adhesive interaction between MPs and the wall. (i) and (iii) promote margination, while (ii) hampers margination. These three factors perform different roles and compete against each other when MPs are located in different regions of the flow channel, i.e. near wall region. In optimal region I, adhesion outperforms deformation induced lift force, and in region II, the deformation induced lift force is small compared to the coupling of hydrodynamic collision and adhesion. More importantly, our results suggest that softer MP or stronger adhesion is not always the best choice for the margination of MPs.

Wednesday 6:30 Woodway II/III

PO109

**Viscosity curve measurements for actual and mimic bloods by originally developed RheoSpec system**Taichi Hirano, Shujiro Mitani, and Keiji Sakai*Fundamental Engineering, Inst Indust Sci, UTokyo, Meguro-ku, Tokyo 153-8505, Japan*

Recently, we developed an epoch-making system for sealable and disposable rheometry, which can obtain viscosity curve even for lowly viscous liquids such as alcohol solutions and biological fluids. The system named Rheology-Spectrometer (RheoSpec) might be a useful tool for pathological tests and medical checks, preventing contamination to/from sample specimens. In the advanced-type of RheoSpec system, a thin aluminum disk is employed as a rotating probe, and the probe is designed so that it automatically stands by the support of the buoyancy from the sample fluids. In addition, the driving principle is the electromagnetically spinning (EMS) technique originally developed by us, and then a controlled remote torque is applied to the probe. Since the mechanical friction is reduced due to these features, high accuracy in measuring lower viscosity can be achieved than the conventional rheometers. Note here that the geometry in the RheoSpec is similar to that in a parallel-plate viscometer. When the flow or viscosity curve is measured by this system, the obtained data under a constant rotational speed contains superposed information on various shear velocities. However, we already validated a numerical procedure to convert the measured data to the exact flow or viscosity curve. In this presentation, we introduce some measured results of viscosity curves for human whole bloods, and discuss the repetition performance as well as individual difference. The measurable range of shear velocity for blood with the RheoSpec system is from 3 to 600  $s^{-1}$ , which covered the typical velocity range of bloodstream in a living body. Furthermore, it can be expanded to lower region, where we expect to observe slow dynamics of degrees of freedom in blood, such as the deformability of red blood cells. Actually the data in the lower region showed clear individual differences, and gives information on the molecular motions of RBCs. We also talk about the comparison results for mimic bloods made by a microdroplet manipulating technique.

Wednesday 6:30 Woodway II/III

PO111

**Multifaceted blood prediction using the Blackwell-Ewoldt thixo-elasto-visco (TEV) and Herschel-Bulkley/Stickel models**Michael Clark and Matthew J. Armstrong*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States*

Many complex materials have thixotropic behaviors, displaying time dependent viscous and elastic properties that are a function of microstructure. Some examples of thixotropic materials are aqueous nuclear waste, crude oil, and paints. Another example is blood. Modeling the behavior of these materials allows us to better understand how they can be used effectively in their respective industry. We have characterized human blood using recently collected steady state data and the Blackwell-Ewoldt TEV model, and Herschel-Bulkley/Stickel models. First, we analyzed steady state data and compared parameter predictions to physiological parameters, then we simultaneously fit the Blackwell-Ewoldt and HB/Stickel model to steady state and a transient sawtooth function again using recently collected blood data. Using the best fit parameter values from the steady state-sawtooth fit, we predicted small amplitude oscillatory shear (SAOS), and LAOS. We also demonstrate and compare using fits with step up/step down transient experiments. We characterize blood to develop better models, and evolve strategies to give way to better understanding of blood to facilitate benchmarking blood's "normal" rheological fingerprint, with a view toward a methodology to diagnose pathologies based on rheological deviations from blood's baseline mechanical properties. Based on the biochemistry of blood, its fluid mechanics, and rheological properties, pathological blood will have different rheological properties than healthy blood. By modeling healthy blood, we can establish a baseline that will then allow us to characterize and diagnose pathological blood based on its flow behavior, as was seen in the Moreno paper with high cholesterol. We then look for statistically significant relationships between certain model parameters and physiological parameters measured from the blood like cholesterol, sugar, hematocrit, etc.

Wednesday 6:30 Woodway II/III

PO112

**Multifaceted blood prediction using the Bautista-Monero-Puig (BMP) model**Keith Charles<sup>1</sup> and Matthew J. Armstrong<sup>2</sup><sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States*

Many complex materials have thixotropic behaviors, displaying time dependent viscous and elastic properties that are a function of microstructure. Some examples of thixotropic materials are aqueous nuclear waste, crude oil, and paints. Another example is blood. Modeling the behavior of these materials allows us to better understand how they can be used effectively in their respective industry. We have characterized human blood using recently collected steady state data and the Bautista-Monero-Puig (BMP) model. First, we analyzed steady state data and compared parameter predictions to physiological parameters, then we simultaneously fit the BMP model to steady state and a transient sawtooth function again using recently collected blood data. Using the best fit BMP parameter values from the steady state-sawtooth fit, we predicted small amplitude oscillatory shear (SAOS), and LAOS. We also demonstrate and compare using fits with step up/step down transient experiments. We characterize blood to develop better models, and evolve strategies to give way to better understanding of blood to facilitate benchmarking blood's "normal" rheological fingerprint, with a view toward a methodology to diagnose pathologies based on rheological deviations from blood's baseline mechanical properties. Based on the biochemistry of blood, its fluid mechanics, and rheological properties, pathological blood will have different rheological properties than healthy blood. By modeling healthy blood, we can establish a baseline that will then allow us to characterize and diagnose pathological blood based on its flow behavior, as was seen in the Moreno paper with high cholesterol. We then look for statistically significant relationships between certain model parameters and physiological parameters measured from the blood like cholesterol, sugar, hematocrit, etc.

Wednesday 6:30 Woodway II/III

PO113

**Multifaceted blood prediction using contemporary thixotropic and viscoelastic models**Michael Clark<sup>1</sup>, Matthew J. Armstrong<sup>1</sup>, and Jeffrey S. Horner<sup>2</sup><sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Many complex materials have thixotropic behaviors, displaying time dependent viscous and elastic properties that are a function of microstructure. Some examples of thixotropic materials are aqueous nuclear waste, crude oil, and paints. Another example is blood. Modeling the behavior of these materials allows us to better understand how they can be used effectively in their respective industry. We have characterized human blood using recently collected steady state data and the Blackwell-Ewoldt TEVP model, and an enhanced Apostolidis-Armstrong-Beris with viscoelastic modification model. First, we analyzed steady state data and compared parameter predictions to physiological parameters, then we simultaneously fit the models to steady state and a triangle ramp and step up/down rheological human blood data. Using the best fit parameter values from the steady state-triangle ramp-step up/down fit, we predict and Large Amplitude Oscillatory Shear flow. We characterize blood to develop better models, and evolve strategies to give way to better understanding of blood to facilitate benchmarking blood's "normal" rheological fingerprint, with a view toward a methodology to diagnose pathologies based on rheological deviations from blood's baseline mechanical properties. Based on the biochemistry of blood, its fluid mechanics, and rheological properties, pathological blood will have different rheological properties than healthy blood. By modeling healthy blood, we can establish a baseline that will then allow us to characterize and diagnose pathological blood based on its flow behavior, as was seen in the Moreno paper with high cholesterol. We then look for statistically significant relationships between certain model parameters and physiological parameters measured from the blood like cholesterol, sugar, hematocrit, etc.

Wednesday 6:30 Woodway II/III

PO114

**Multifaceted blood prediction using the Horner-Armstrong-Wagner-Beris thixo-elasto-visco-plastic (TEVP) model**Michael Deegan<sup>1</sup>, Matthew J. Armstrong<sup>1</sup>, and Jeffrey S. Horner<sup>2</sup><sup>1</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Many complex materials have thixotropic behaviors, displaying time dependent viscous and elastic properties that are a function of microstructure. Some examples of thixotropic materials are aqueous nuclear waste, crude oil, and paints. Another example is blood. Modeling the behavior of these materials allows us to better understand how they can be used effectively in their respective industry. We have characterized human blood using recently collected steady state data and the Horner-Armstrong-Wagner-Beris TEVP model. First, we analyzed steady state data and compared parameter predictions to physiological parameters, then we simultaneously fit the HAWB model to steady state and a series of triangle ramp functions again using recently collected blood data. Using the best fit HAWB parameter values from the steady state-sawtooth fit, we predict Large Amplitude Oscillatory Shear flow. We also demonstrate and compare using fits with step up/step down transient experiments. We characterize blood to develop better models, and evolve strategies to give way to better understanding of blood to facilitate benchmarking blood's "normal" rheological fingerprint, with a view toward a methodology to diagnose pathologies based on rheological deviations from blood's baseline mechanical properties. Based on the biochemistry of blood, its fluid mechanics, and rheological properties, pathological blood will have different rheological properties than healthy blood. By modeling healthy blood, we can establish a baseline that will then allow us to characterize and diagnose pathological blood based on its flow behavior, as was seen in the Moreno paper with high cholesterol. We then look for statistically significant relationships between certain model parameters and physiological parameters measured from the blood like cholesterol, sugar, hematocrit, etc.

Wednesday 6:30 Woodway II/III

PO115

**Stress-stabilized sub-isostatic rope networks**Sadjad Arzash<sup>1</sup>, Jordan Shivers<sup>1</sup>, Albert J. Licup<sup>2</sup>, Abhinav Sharma<sup>3</sup>, and Fred C. MacKintosh<sup>1</sup><sup>1</sup>*Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States;* <sup>2</sup>*Department of Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands;* <sup>3</sup>*Leibniz Institute for Polymer Research, Dresden 01069, Germany*

Sub-isostatic biopolymer networks with only central force interactions exhibit a mechanical phase transition from floppy (unstable) to rigid state under simple shear deformation. Introducing weak bending interactions stabilizes these networks and decreases the critical signatures of this transition. We show that applying large enough external normal stresses on a sub-isostatic network with only tensile central force interactions (rope limit) also stabilizes the networks and removes the criticality. Moreover, for small prestresses, we find a sub-linear scaling relation between linear shear modulus and the prestress. Interestingly, this power-law exponent appears to be independent of network's connectivity. We also find an increasing shift in the onset of strain stiffening under simple shear deformation by applying external stresses.

Wednesday 6:30 Woodway II/III

PO116

**Measurement of blood-coagulation-process by new lineup of EMS (Electro-Magnetically-Spinning) rheometer**Yoshikazu Yamakawa<sup>1</sup>, Yoji Okada<sup>1</sup>, and Keiji Sakai<sup>2</sup><sup>1</sup>*Triple Eye Co. Ltd., Kyoto, Japan;* <sup>2</sup>*Fundamental Engineering, Inst Indust Sci, UTokyo, Meguro-ku, Tokyo 153-8505, Japan*

EMS(Electro-Magnetically-Spinning) viscometer developed by us can measure the viscosity in a non-contact manner: rotating magnetic field induces current in a metal rotation probe set in the sample and the Lorentz interaction between the magnetic flux and the current drives the rotation of the probe. Viscosity and its dependence on shear rate can be obtained from the relation between the rotational speeds of the magnetic field and the probe. Thus, "Non-Contact", "Sealable", "Disposable", "Safe" measurements are known as the big key features of EMS method especially for the medical field since such samples as blood can be bio-hazardous. Lately, we improved the system to detect the elastic modulus of the sample by applying an alternative torque. In this session, we present the new possibility of "Blood Coagulation Process Measurement based on rheological approach" utilizing the latest rollout of EMS Rheometer.

Wednesday 6:30 Woodway II/III

PO117

**Surface-induced drag on motile bacteria**Ravi Chawla, Rachit Gupta, Katie M. Ford, and Pushkar P. Lele*Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, United States*

Surface-dependent collective motility of elongated, flagellated bacteria known as swarming represents an important mechanism for colonies to effectively cover large distances on soft surfaces and tissues. Swarming, involved in urinary tract infections, is likely initiated when the flagella sense higher viscous loads such as those experienced near solid boundaries. As cells of *E. coli* transition into the swarmer state, they develop twice as many flagella to overcome the surface drag. However, the underlying assumption that soft agar surfaces result in high loads on the flagella remains untested. Here, we developed an approach to estimate the hydrodynamic drag as a function of separation from soft-agar interfaces. In one type of testing, the surface-induced load on the flagellar motor was interpreted from the rates of swarming in two strains that developed differential motor-power as a function of load. In the second type of testing, blinking optical tweezers were employed to estimate the diffusivities of latex beads as a function of separation from agar interfaces. The results are anticipated to help test the hypothesis that a higher viscous drag on the flagella functions as an extracellular signal to initiate the transition to the swarmer state.

Wednesday 6:30 Woodway II/III

PO118

**Flow of biopolymer-based microcapsules through a constriction**Bruna C. Leopércio, Mariano Michelon, and Marcio S. Carvalho*Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451900, Brazil*

The flow of soft particle and microcapsule suspensions through confined spaces is important in many fields, including enhanced oil recovery, reactor feeding, red-blood-cell transport and drug delivery. In the particular case of enhanced oil recovery, the reduction of the water phase mobility by the addition of small amounts of soft microcapsules can lead to flow diversion and an increase on the volume of displaced oil. We produced biopolymer-based microcapsules with tunable physical parameters, including shell thickness and elastic modulus, to better control the flow of the suspensions through constricted spaces. The microcapsules are produced by capillary microfluidics, which combine co-flow and flow-focusing in coaxial glass-capillaries, to prepare batches of biopolymer-based microcapsules using gellan gum and sunflower oil. Adjusting the fluid flow rates and the biopolymer/gelling agent ratio enabled the production of microcapsules with the same diameter but tunable mechanical properties. The effect of these properties on the flow resistance is studied by measuring the extra pressure drop associated with the flow of single suspended microcapsules through constrictions; the shell thickness has a strong effect on the flow mobility. The results show how microcapsules can be designed and produced to achieve the desired suspension flow behavior in porous media.

Wednesday 6:30 Woodway II/III

PO119

**An interspecies comparison of blood rheology**Jeffrey S. Horner<sup>1</sup>, Antony N. Beris<sup>1</sup>, Norman J. Wagner<sup>1</sup>, and Donna S. Woulfe<sup>2</sup><sup>1</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States;* <sup>2</sup>*Biological Sciences, University of Delaware, Newark, DE, United States*

Despite almost always containing the same constituents, blood from different species may exhibit significantly different rheological profiles. These differences are primarily attributed to changes in the red blood cell interactions across species. Most notably, red blood cells from some species such as human, pig, and horse may reversibly aggregate at low shear rates to form coin stack structures called rouleaux. However, this phenomenon is absent in blood from other species such as sheep, cow, and chicken. When rouleaux are present, the viscosity of the blood will significantly increase at low shear rates and the blood may exhibit a nonzero yield stress. Moreover, due to the reversible nature of this aggregation process, blood samples in which rouleaux are present will exhibit thixotropy. In this work, we present new steady and transient rheological data on blood from various species. Using the acquired data, we fit a modified version of a recently published blood thixotropy model to demonstrate the universality of the model and quantify the differences between the various species sampled [1]. This study raises some interesting and clinically relevant questions pertaining to the causes of rouleaux formation from both an evolutionary and biological viewpoint. Understanding this phenomenon is important as a number of diseases have been linked to enhanced rouleaux formation. Moreover, by understanding the changes in blood rheology across species we can improve the scale up process for intravenous drugs as a number of drugs are first tested on animals.

[1] Horner et al., *J. Rheol.*, 62(2), (2018).

Wednesday 6:30 Woodway II/III

PO120

**Non-equilibrium deformation and relaxation of giant floppy vesicles in a precisely controlled extensional flow**Dinesh Kumar and Charles M. Schroeder*Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

In this work, we study the non-equilibrium dynamics of single floppy vesicles under large strain rates ( $\sim 15 \text{ s}^{-1}$ ) using a Stokes trap, which is a new technique developed in our lab for controlling the center-of-mass position of multiple particles or single molecules in a free solution. In this way, we directly observe the vesicle shape and conformations as a function of reduced volume, which is a measure of a vesicle's equilibrium shape departure from sphericity. We observe the formation of asymmetric dumbbell shapes, pearling, and wrinkling and buckling instabilities for vesicles depending upon the nature of flow and amount of membrane floppiness. We report the precise stability boundary of the flow-based phase diagram for vesicles in Capillary number ( $Ca$ )-reduced volume space, where  $Ca$  is the ratio of the bending time scale to the of flow time-scale. We further probe the stability boundary at two different viscosity ratios to understand how the onset of asymmetric instability in vesicles depends on viscosity ratio. We also present results on the long-time relaxation dynamics of vesicles from high deformation back to their equilibrium spheroidal shapes after the cessation of flow. We study vesicles with shapes ranging from symmetric to asymmetric dumbbells with a long thin tether (extremely large fractional extensions with flattened thermal fluctuations), and we report on the influence of initial conditions in determining dynamic behavior. Overall, our results provide new insights into the flow-driven shape-instabilities for vesicles which has been achieved using new experimental methods involving the Stokes trap and related precise control over the center-of-mass position of vesicles, resulting in observation times on order of the time required for instabilities to form.

Wednesday 6:30 Woodway II/III

PO121

**Dynamics and structure of active fluids under confinement**Tong Gao*Mechanical Engineering, Michigan State University, East Lansing, MI 48824, United States*

We numerically study the dynamics and structure of a simple apolar active fluid under confinement through an active liquid crystal model. At the micro scale, we consider a suspension comprises microparticles that are nonmotile but mobile, and exert active dipolar stresses on the ambient liquid. We show that such a system can be described by a coarse-grained liquid crystal model that is derived from a microscopic Doi-Onsager kinetic theory. Then we use the macro model to study the collective dynamics of the apolar fluid confined in straight, circular and bi-concave geometries. We also explore the soft confinement effect by encapsulating a dense active suspension in a droplet whose motion is driven by the internal active nematic flows.

Wednesday 6:30 Woodway II/III

PO122

**Delivering active motion to colloidal gels for microdynamics and mechanical rheometry measurements**Keara T. Saud<sup>1</sup>, Megan E. Szakasits<sup>2</sup>, and Michael J. Solomon<sup>2</sup><sup>1</sup>*Materials Science and Engineering, University of Michigan, Ann Arbor, MI, United States;* <sup>2</sup>*Chemical Engineering, University of Michigan, Ann Arbor, MI 48105, United States*

We explore the effects of embedded active colloids in fractal cluster colloidal gels. These gels are a model system whose structure, dynamics, and rheology are all well characterized. Broadly, colloidal gels are a space-spanning network of particles arrested in a liquid because of strong and short-ranged attractive interactions. Control of the mechanical properties of gels is potentially applicable to industrial applications of gels including, paints and coatings, pharmaceuticals, or agricultural formulations. One potential strategy to tune the mechanical properties of gels is to use active matter- a field of non-equilibrium and self-propelling motion - in the gel. Active matter uses local gradients induced by asymmetric

reactions, electric fields, light or other external fields to generate unique motion, such as spinning, swarming, and clustering. Here we embed active particles into colloidal gels to probe the effects on gel dynamics and rheological properties. Because current methods for delivery of active motion present challenges for rheological experiments, we introduce two different approaches to overcome these challenges for active colloidal gel systems. Specifically, we use two different mechanisms to generate active motion - self-diffusiophoresis induced by hydrogen peroxide and induced-charge electrophoresis generated with AC electric fields. Using the techniques we developed, we were able to measure the viscoelastic moduli of active colloidal gels. We find the addition of active motion into colloidal gels enhances the dynamics of the gel network, which has implications for the mechanical properties of the gel.

Wednesday 6:30 Woodway II/III

PO123

### **Extensional rheology of human whole saliva and the role of the particulate matter**

Naureen S. Suteria<sup>1</sup>, Stefan Baier<sup>2</sup>, and Siva A. Vanapalli<sup>1</sup>

<sup>1</sup>Texas Tech University, Lubbock, TX, United States; <sup>2</sup>PepsiCo., Hawthorne, NY 10532, United States

Saliva is an important mucous biofluid that is essential for macerating and swallowing food as well as maintaining oral health by reducing the risk of oral infection and tooth decay. Saliva is one of the most researched biofluids due to its ease of collection and accessible sample volumes. However, it is a complex fluid containing mucins, proline-rich proteins, enzymes, and epithelial cells that not only varies between individuals, but can also vary between different times for the same individual. There has been significant work on the shear rheology of human whole saliva that was collected under different stimulated conditions, but the literature is heavily lacking in studies of saliva's extensional rheology. There are only a handful of studies done, with very limited sample sizes, and inconsistent handling protocols. The extensional rheology of a dilute viscoelastic fluid is sensitive to how it is handled and processed as well as it can degrade rapidly in a short amount of time. Many studies on rheology will simply remove the large particulate matter, by centrifugation or filtration, so that they have an easier to test aqueous sample. However, in this study we show that the particulate matter plays a significant role in the extensional behavior of saliva and removing it reduces the sample's elastic properties. We used dripping-on-substrate rheology to measure the relaxation time and extensional viscosity of freshly collected stimulated and rested saliva as well as filtered and centrifuged samples. We discuss the effects of the particle size distribution and concentration on the extensional rheology.

Wednesday 6:30 Woodway II/III

PO124

### **Effect of SiO<sub>2</sub>-based nanofluids in the reduction of naphtha consumption for heavy and extra-heavy oils transport: Economic impacts on the Colombian market**

Esteban A. Taborda Acevedo<sup>1</sup>, Farid B. Cortes Correa<sup>1</sup>, Vladimir Alvarado<sup>2</sup>, and Camilo A. Franco Ariza<sup>1</sup>

<sup>1</sup>Grupo de Investigación en Fenómenos de Superficie. Michael P, Universidad Nacional de Colombia sede Medellín, medellin, Antioquia 050036, Colombia; <sup>2</sup>Department of Chemical Engineering, Dept. 3295., University of Wyoming, Laramie, WY 82071, United States

Techniques commonly used to improve the heavy crude oil transport includes the addition of solvents, as they contribute to reducing oil viscosity. However, the high consumption of these solvents increases transportation costs and generates different environmental risks, making it an unattractive technique. The objective of this study is to evaluate the effect of nanofluids as additives to optimize the transport of heavy crude oil using steady-state rheological measurements and dynamic flow tests. The use of these additives produces viscosity reduction for heavy (HO) and extra heavy (EHO) crude oils. Four nanofluids were prepared using different solvents and fumed silica nanoparticles. Mixtures with naphtha were prepared to reduce the viscosity of the crude oil as to attain mobility targets (400-500 cP at 311K). To this end, 27% and 63% v/v of naphtha were required for heavy and extra-heavy crude oils, respectively. Steady-state rheological measurements were conducted at 311K, and the best performing material turned out to be the nanofluid composed of 1000 mg/L of SiO<sub>2</sub> and biodiesel. This nanofluid yielded a reduction in the consumption of naphtha of approximately 50%. Consequently, dynamic flow tests in a pipeline were conducted at 298 and 313K for both crude oils. The same pressure differential was obtained by adding 10% of the nanofluid and reducing the consumption of naphtha by more than 50% in all mixtures. Our results show that the best-performing nanofluid can serve as an optimizing agent for the transport conditions of heavy and extra-heavy crude. The proposed technology was evaluated through an economic analysis that shows a potential reduction of dilution costs of almost 50%, equivalent to more than USD \$2.5 million per day, as well as a decreased energy consumption. Additionally, a discussion on environmental impacts are presented. A nanofluid-based technology could generate savings in both energy and fuel consumptions.

Wednesday 6:30 Woodway II/III

PO125

### **Innovative rheology method for barite sagging prediction**

Yan Gao<sup>1</sup>, Yiyang Chen<sup>2</sup>, and Reda Karoum<sup>2</sup>

<sup>1</sup>Schlumberger, Sugar Land, TX, United States; <sup>2</sup>Schlumberger, Houston, TX, United States

In the past, drilling fluids engineers relied on viscosity at low shear rate or gel strength measured by conventional API methods as an indication for barite sag tendency. However, a significant number of studies have shown that the near-static sag behavior is not well correlated to rheology parameters (yield point, plastic viscosity, gel strength) measured this way. An in-depth investigation, studying the rheological properties of various drilling fluids utilizing both flow ramp and oscillation tests was conducted. This resulted in one rheological parameter of 16-hour heat aged samples showing a high linear correlation to the density differences measured after 7-day aging. As drilling technology has advanced, the use of extended reach drilling has become a norm in achieving economic success during development drilling. There is a desire to develop standard practices to minimize drilling risk, in particular that related to narrow pressure margins. One of the challenges faced is the potential for barite sagging due to drilling fluid instability created by long circulation periods without high shear. If barite sagging occurs, the density gradient of

fluid form along the wellbore. The resulting pressure differential can lead to loss of circulation, wellbore collapse or well control problems. In this context, engineers need to design drilling fluids with the ability to fully suspend barite particles at elevated temperature under static conditions for extended reach, deep water, or HPHT wells. Drilling fluids are currently designed based on specific chemical selection guidelines and are refined via laboratory testings directed towards wellsite performance prediction. Among these tests, static sag analysis requires a 7-day aging period of the fluid. It is one of the most crucial tests and can also be a bottle neck for formulation optimization. Until recently, there has been no rapid method that can accurately predict the long term, near static, sag behavior of the fluid formulations.

Wednesday 6:30 Woodway II/III

PO126

### **Microstructure of SBS modified asphalt binder by small-angle neutron scattering**

Liyan Shan<sup>1</sup>, Ru Xie<sup>2</sup>, Norman J. Wagner<sup>3</sup>, and Yun Liu<sup>4</sup>

<sup>1</sup>*School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin, China;* <sup>2</sup>*University of Delaware, Newark, DE, United States;* <sup>3</sup>*University of Delaware, Newark, DE, United States;* <sup>4</sup>*Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, United States*

The microstructure of asphalt binders is thought to have a significant effect on the performance of binders used in roadway construction, however, there are limited studies of their nanoscale to microscale structure. Here, small angle neutron scattering (SANS) is used to study the microstructure of neat asphalt binder, SBS polymers and SBS modified asphalt binder. The results show that the micelle in asphalt binders was plated-shape and the size was larger than 1800 Å. Both the intensity curve and the rheology results showed that SBS modified asphalt has a phase transition temperature around 110°C, while the SBS micelles swell and loose contrast above this temperature. The thermal reversibility of this phenomenon proves that the SBS modified mechanism is a physical modification of the microstructure as proposed in the colloidal model of asphalt. Modeling of the SANS spectra shows that both SBS polymer and SBS in asphalt binder have a lamellar structure surrounding by a shell. The results of this paper are useful to analyze the relationship between microstructure of asphalt binder and pavement performance and develop a new type of modified asphalt binder.

Wednesday 6:30 Woodway II/III

PO127

### **Altering wax appearance using shear and pressure**

Abdualbaset Ali, Uchenna Asogwa, Kayla Piezer, and Matthew W. Liberatore  
*Chemical Engineering, University of Toledo, Toledo, OH 43606, United States*

Oil and gas flow inside pipelines are vital to supply the world's energy in the 21<sup>st</sup> century. Waxes are common component in crude oils, which can precipitate during production and transport causing cessation of flow. Wax appearance creates maintenance and safety concerns as well as economic losses in crude oil handling. Therefore, understanding wax appearance under flow could benefit the fuels industry broadly. In this work, a model wax-oil system with different wax contents is examined using rheology and phase behavior. The effect of shear on the wax appearance temperature as a function of wax concentration and pressure, and comparing the results with the same measurement at static condition. A high-pressure rheology system, which was previously commissioned to study methane hydrates, can alter pressure and thus concentration of methane of a waxy oil. A wax appearance phase diagram with temperature, shear, and pressure as independent variables is being established. Rheological measurements of waxy oil samples will use both parallel plate and cup and bob geometries across shear rates from 1 to 1000 s<sup>-1</sup>. Finally, the wax appearance will be monitored using in situ small angle light scattering with rheology to determine if torque or scattered light identifies wax appearance earlier.

Wednesday 6:30 Woodway II/III

PO128

### **Characterizing the wear behaviors of carrageenan and whey protein isolate gels by numerical modeling**

Juzhong Tan and Helen S. Joyner

*Food Science, University of Idaho, Moscow, ID 83844-2312, United States*

Hydrogels are soft materials that have many medical and industrial applications such as contact lenses and artificial cartilage. Because hydrogel friction/wear behaviors may be indications of their durability, elasticity, and deformability, wear models can help predict the lifetime of the hydrogel as a bearing surface. Thus, the objective of this study was to characterize the wear behavior of hydrogels using a numerical model. Tribological tests were conducted using a twin-ball-on-disk geometry. Wear behaviors of whey protein isolate (WPI), carrageenan and mixed WPI/carrageenan gels with different carrageenan concentration (0.3-1.0% w/w) and ionic strength (50-150mM) were evaluated. The numeric model characterized both deformation and wear of gels by four parameters:  $R(1,i=1)$ ,  $d1$ ,  $R(2,i=8)$ , and  $d2$ .  $R(1,i=1)$  is penetration depth per unit (normal) force, indicating how easily the sample can be deformed under a given normal force.  $R(2,i=8)$  is the penetration depth per unit (frictional) force, reflecting the constant wear rate after an infinite number of contacts.  $d1$  and  $d2$  are the rate of change for  $R(1,i=1)$  and  $R(2,i=8)$ , respectively. All models had mean absolute error <16  $\mu\text{m}$  indicating good fit. Increased normal force generally increased the  $R(1,i=1)$ ,  $d1$  and  $d2$  values of all gel models, implying that increased normal force caused increased and deformation and deformation rate. However, increased normal force did not result in increased  $R(2,i=8)$  values, which indicated that increased normal did not necessarily impact wear rates. Both polymer concentration and gel ionic strength impacted  $R(1,i=1)$ ,  $R(2,i=8)$ ,  $d1$ , and  $d2$  values; the effects were dependent on how these parameters impacted gel microstructures and fracture energies. The model developed in this study can be used by researchers and food, bioprocessing, and pharmaceutical product manufacturers to develop structure-function-texture relationships for their products and evaluate the suitability of new formulations for various applications.



Wednesday 6:30 Woodway II/III

PO129

**An insight into linear and non-linear behaviour of microfibrillated cellulose suspensions**Sweta Sarangi and Suresh K. Yatirajula*Chemical Engineering, Indian Institute of Technology ISM Dhanbad India, Dhanbad, Jharkhand 826004, India*

Microfibrillated Cellulose, being a new class of novel material extracted from plants and agricultural residues through various techniques such as high pressure homogenisation, ultrasonication, cyrocrushing, grinding, chemical treatment and possessing multifaceted properties such as large surface area, high aspect ratio, mechanical robustness, biodegradability, biocompatibility, barrier to oxygen, complex rheology has drawn a lot of attention in last decade. It is quite interesting to observe that Microfibrillated Cellulose suspension exhibits an extreme pseudoplastic behaviour and viscoelastic properties even at very low concentration also. In this work, the effect of temperature and concentration on the suspension of MFC were studied. Three zones of MFC were observed for the shear rate range of 0.01s<sup>-1</sup>-1000 s<sup>-1</sup> which is supported by build up of network of hydroxyl groups present on the surface, resulting in dilatant behaviour. With the rise in concentration of MFC, there was rise in viscosity as well as storage modulus. Higher value of storage modulus indicated the high degree of cross linking of fibrils. Temperature did not have any significant effect on the MFC varying from 25 °C- 60 °C. Dynamic Oscillatory measurements were performed to validate the viscoelastic behaviour. MFC displayed linear behaviour in the range of 0.07% of strain amplitude with the cross-over of frequency of 10% of strain amplitude. Storage modulus was observed to be independent of frequency. To track the non-linearity in the behaviour, study of LAOS was conducted. From the Lissajous-Bowditch curve the, non-linear viscoelastic parameters revealed the elastic non-linearity in the material in the oscillatory cycle. From the close inspection of the LAOS data, the difference in the viscoelastic non-linearity in MFC can be used as a tool to create non-linear rheological fingerprints by providing a new insight into the dynamics of non-linearity.

KEYWORDS: Microfibrillated Cellulose, Pseudoplastic, Viscoelastic, LAOS

Wednesday 6:30 Woodway II/III

PO130

**Electrorheology in food science: Tweaking the viscosity of liquid Chocolate by Electrocution!**Kazi M. Tawhid-Al-Islam, Hong Tang, Enpeng Du, and Rongjia Tao*Department of Physics, Temple University, Philadelphia, PA 19122, United States*

Chocolate is one of the most popular food types and flavors in the world. During the manufacturing processes into the end consumer grade products, chocolate is liquid, which is a suspension of solid particles consisting of cocoa, sugar, milk solids etc. in a base liquid of melted fat and oil, mainly cocoa butter. Viscosity of liquid chocolate is a very critical quantity that determines production cost. Whereas, viscosity depends on the fat content in chocolate. Reducing the fat level would make the chocolates much healthier, however, removing even a small amount of fat would make chocolate very thick and viscous, and would be very difficult to maneuver through pipelines. Here we will present an innovative method to tackle this challenge from the basic science of liquid suspension, especially, tweaking its viscosity and maximally random jammed (MRJ) density with the unconventional use of electrorheology (ER). When electric field is applied along the flow direction, the cocoa particles, typically of spherical shape, form short chains and behave as prolate spheroids. This microstructure change breaks the rotational symmetry, leading to increased MRJ, thus viscosity reduces substantially along the flow direction. Therefore, the viscosity of the chocolate composed of less fat can be brought down with ER treatment matching the viscosity of regular composition, resulting favorable condition for production. Hence, we expect a new class of healthier low-fat chocolate soon.

Wednesday 6:30 Woodway II/III

PO131

**Relating cheese wear to its rheological and sensory behaviors**Fariba Zad Bagher Seighalani<sup>1</sup> and Helen S. Joyner<sup>2</sup>*<sup>1</sup>School of Food Science, University of Idaho, Moscow, ID 83844, United States; <sup>2</sup>University of Idaho, Moscow, ID 83844-2312, United States*

Determination of how foods deform and break down is important for understanding both their processing behaviors and texture attributes. The objective of this study was to determine relationships among rheological behaviors, wear behaviors, and sensory texture cheese. Full-fat cheeses with 50% and 54% fat (dw) and reduced fat cheese with 28% fat (dw) were evaluated. Wear measurements were performed at 0.5 N normal force, 50 mm/s sliding speed, and different temperatures (5, 15 and 25°C). Large amplitude oscillatory shear (LAOS) and strain sweep tests were used to measure cheese rheological properties. A descriptive sensory analysis was used to evaluate cheese sensory textural attributes. Cheeses containing 54% (dw) fat had significantly higher penetration depth at all conditions compared to cheeses with lower fat content. Reduced-fat cheese showed significantly lower mass loss (wear) in all conditions compared to full-fat cheeses. Lower rigidity at higher temperatures led to greater penetration depth in all cheeses. Lissajous curves showed that cheeses had greater deformation at higher strains. Sensory results showed significantly higher fracturability, number of particles, and firmness, and lower cohesiveness, smoothness, adhesiveness, moistness, mouth-coating, rate of recovery, and springiness in reduced-fat compared to full-fat cheeses. Lower wear was correlated to higher moduli values and high sensory first-bite firmness, hand firmness, and fracturability (R<sup>2</sup>=0.81 to 0.87). The findings of this study provided a fundamental understanding of the effect of fat content on relationships among cheese rheological properties, wear behavior and sensory attributes.

Wednesday 6:30 Woodway II/III

PO132

**Rheological behavior of aqueous solutions of Nopal mucilages with different molecular weight**Francisco Rodríguez-González<sup>1</sup>, José Pérez-González<sup>2</sup>, and Benjamín M. Marín-Santibáñez<sup>3</sup><sup>1</sup>*Departamento de Biotecnología, Instituto Politécnico Nacional, Yautepec, Morelos 62731, Mexico;* <sup>2</sup>*Laboratorio de Reología y Física de la Materia Blanda, Instituto Politécnico Nacional, Ciudad de Mexico 07738, Mexico;* <sup>3</sup>*SEPI-ESIQIE, Instituto Politécnico Nacional, Ciudad de Mexico 07738, Mexico*

*Opuntia ficus indica* (Nopal) is cultivated in different countries for alimentary and industrial purposes. The mucilage obtained from Nopal is a branched polysaccharide of high-molecular weight, which is water soluble and may form viscous and viscoelastic solutions, depending on its molecular weight and concentration. Due to these facts, Nopal mucilages may be used as rheological modifiers. Despite the large amount of practical applications of Nopal, there is a dearth of systematic studies about the rheological behavior of its mucilage solutions. In this work, a study of the effect of different maturation ages of Nopal (cladodes) on the molecular weight of its mucilage and shear flow behavior in solution was performed. The weight-average molecular weight ( $M_w$ ) of the mucilages and the second virial coefficient were determined at a temperature of 25 °C by dynamic light scattering and the different concentration regimes were calculated. Steady and dynamic shear flow experiments were performed by using a stress-controlled rheometer at a temperature of 25 °C with the cone and plate and Couette geometries. Aqueous mucilage solutions were prepared at concentrations of 2, 4 and 6 wt.%, respectively from cladodes having ages of 20, 40 and ~600 days, respectively. It was found that increasing the maturation age resulted in increased  $M_w$  of the mucilages, with the concomitant effect on concentration regimes and viscosity. Solutions prepared with mucilage from young cladodes did not exhibit elasticity, meanwhile those from the old ones showed highly elastic behavior for concentrations = 4 wt.%. Finally, mucilage solutions at 4 and 6 wt.% from the oldest cladodes behaved as weak gels and exhibited yield stress.

Wednesday 6:30 Woodway II/III

PO133

**Thermal and viscoelastic behavior of polymer films used as photovoltaic module encapsulants**Ashley M. Maes, James Y. Hartley, and Christine C. Roberts*Sandia National Laboratories, Albuquerque, NM, United States*

As the photovoltaic (PV) industry continues to mature and expand rapidly, prediction of module durability and lifetime has become a key area of focus. This work is part of an effort to develop a multi-scale thermal-mechanical finite element model to predict mechanical stresses within PV modules that lead to package degradation. The polymer encapsulant layer of PV modules acts as a binder between cover glass, solar cells and polymer backsheet layers while providing mechanical stability and protection of cells and interconnects from the outdoor environment. The viscoelastic nature of these encapsulants is suspected to be a key factor affecting component stress states, and thus further experimental characterization was warranted to populate a representative constitutive model for finite element simulations.

In the presented work, the thermal transitions and linear viscoelastic behavior of commercial poly(ethylene-vinyl acetate) (EVA) and polyolefin elastomer (POE) films were studied using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Prior to characterization with DMA, the films were heated and pressed to mimic lamination conditions used during module manufacturing. Complex moduli collected from isothermal frequency sweeps between -40 °C to 30 °C were shifted to produce master curves for each material and a generalized Maxwell model was fit to each curve. Resulting parameters and quality of fit will be included, as well as possible strategies to address variations due to extent of cure, polyethylene crystallization/melting, and aging.

\* Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

# Gallery of Rheology

## Symposium GR Gallery of Rheology Contest

Organizers: Randy Ewoldt and Vivek Sharma

Wednesday 6:30 Woodway Foyer

GR1

### **Eye of Sauron**

Alan R. Jacob, Lilian C. Hsiao, and Michael Dickey

*Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United States*

Gallium is a liquid metal that form an elastic native oxide skin. The oxide skin surrounding the liquid metal manifest creases on the air-liquid metal interface. A high energy Concentric Backscattering Detector (CBS) is used to obtain an electron microscopy image which captures an enhanced contrast image of the wrinkles present on the interface. The crinkles resemble fiery flames, when false color is applied. This image reveals the rich interfacial phenomenon displayed by liquid metals which is yet to be properly understood.

Wednesday 6:30 Woodway Foyer

GR2

### **The ins and outs of elastic instabilities in cross-slot flows: A 3D experimental view**

Boyang Qin<sup>1</sup>, Ranjiangshang Ran<sup>2</sup>, Paul F. Salipante<sup>3</sup>, Steven Hudson<sup>3</sup>, and Paulo E. Arratia<sup>2</sup>

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It is well known that polymer molecules can be strongly stretched (and compressed) by the hyperbolic point of a cross-slot flow. Molecules exert forces back on the fluid and, at a critical Weissenberg number ( $Wi$ ), this lead to a symmetry breaking flow instability in the plane of extension. As the  $Wi$  is increased even further, this symmetry breaking instability becomes time-dependent. Here, we use a three-dimensional (3D) holographic particle tracking technique to visualize the flow and find a *new symmetry-breaking instability* to the extension plane, marked by bi-stable flow switching and “buckling” of the separatrix between the impinging streams. Our results shows that in the polymer game of chicken, escape routes are highly three-dimensional.

Wednesday 6:30 Woodway Foyer

GR3

### **Visualization of filament extension atomization using contrast agents and high speed video photography**

Ravi Neelakantan<sup>1</sup>, David Johnson<sup>1</sup>, Jerome Unidad<sup>1</sup>, Elif Karatay<sup>2</sup>, and Eric Cocker<sup>2</sup>

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A model fluid composed of poly(ethylene oxide) is dissolved in a white aqueous suspension at 0.5% wt. to yield a high contrast fluid for high speed video photography of Filament Extension Atomization. The images and photographs are used to visualize flow fields and filament break-up behavior, and are pivotal in the troubleshooting and optimization of process conditions. When formulations cannot be modified, various other lighting techniques are employed to obtain the highest contrast.

Wednesday 6:30 Woodway Foyer

GR4

### **Air invasion into an elasto-viscoplastic fluid in a Hele-Shaw cell: Snowflake**

Behbood Abedi, Bruno da Silva Fonseca, and Paulo R. de Souza Mendes

*Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, RJ, RJ 22451900, Brazil*

We experimentally investigate the Saffman-Taylor instability of air invasion into an elasto-viscoplastic fluid confined in a circular Hele-Shaw cell. The results show a decrease of the finger width for large values of the injection rate. In this study, air invades a Carbopol solution at an excessive velocity, thus the viscous fingering gives us this fascinating snowflake pattern.

Wednesday 6:30 Woodway Foyer

GR5

### **Invasion of miscible fluids into a “real” yield stress fluid**

Marjan Zare and Ian A. Frigaard

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As a simplified model for understanding invasion of fluids into cemented wellbores, we study the invasion of a series of miscible fluids into a vertical column of yield stress fluid using experimental method. The experiment consists of gradually increasing the applied pressure within the

invading fluid “pore” until the fluid enters the column. Observed experimental behaviours in yielding/invasion show that this transition does not occur at a single point, but instead over a stress plateau/range, corresponding to progressive transition between elastic deformation and viscous flow.

Yielding/invasion consists of a complex sequence of stages, starting with a mixing stage, through invasion and transition, to fracture propagation and eventual stopping of the flow. Precise detection of invasion and transition pressures is difficult. Invasion proceeds initially via the formation of a dome of invaded fluid that grows in the transition stage. The transition stage appears to represent a form of stress relaxation, sometimes allowing for a stable dome to persist and at other times leading directly to a fracturing of the gel. The passage from initial invasion through to transition dome is suggestive of elasto-plastic yielding, followed by a brittle fracture.

Wednesday 6:30 Woodway Foyer

GR6

### **Viscoelastic fishbones**

Bavand Keshavarz, Michela Geri, and Gareth H. McKinley

*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Using a novel high-speed photography technique we visualize the interaction between two colliding viscoelastic jets. At different regimes of flow rate, geometrical configurations and liquid viscoelasticity we observe a variety of interesting morphologies. Finally, we focus on a certain regime of parameters for which the formed fluid structure resembles a fishbone. Because of the control on the size distribution of the generated droplets, this phenomenon can have applications in micro-droplet generation or emulsification processes.

Wednesday 6:30 Woodway Foyer

GR7

### **Thixotropy visualized with splashing droplets**

Samya Sen, Anthony G. Morales, and Randy H. Ewoldt

*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

We visualize thixotropy by showing how droplet impact and splashing are significantly affected by aging. Rejuvenated “young” drops splash, whereas aged “old” drops do not. The results were discovered while studying how thixotropy plays a role in spraying, splashing, and coating with yield-stress fluids, using high-speed video observations. The results are scientifically significant because they show how existing dimensionless groups must be modified to include the effect of thixotropy. Educationally, the images represent a unique way to visualize thixotropic aging, a key phenomenon of rheology that has traditionally been difficult to visualize in static images.

Wednesday 6:30 Woodway Foyer

GR8

### **Isolating vibration with viscoelastic fluids**

Tristan Antonsen, R. E. Corman, and Randy H. Ewoldt

*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

The vibration behavior of viscoelastic fluids depends on the frequency of the driving vibration. When vibrating a viscoelastic material at a frequency higher than its characteristic cross-over frequency ( $\omega_c=1/\lambda$ ) where  $\lambda$  is the characteristic relaxation time of the material), the storage modulus is dominant over the loss modulus. A sample that would otherwise look liquid-like will behave in a solid-like manner. Here, a transiently cross-linked polymer (PVA-Borax) is oscillated vertically (using a 9mm offset-mass vibrating motor) at approximately 80 Hz while its characteristic crossover frequency is 7 Hz. The sample acts like a soft solid and is able to form and maintain interesting surface topography.

Wednesday 6:30 Woodway Foyer

GR9

### **Go with the flow**

Michela Geri, Bavand Keshavarz, and Gareth H. McKinley

*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

The rheological behavior of many complex fluids is strongly dependent on the rearrangements that happen to their microstructural constituents, such as solid particles and polymer chains, as they interact with each other and with the continuous solvent phase. It is known that polymer chains can stretch upon elongation, while micrometric non-spherical particles tend to align with the shear flow. In this work we take advantage of full-field high-speed birefringence imaging to visualize how these rearrangements take place under different flow conditions, giving rise to striking pictures of the otherwise hidden local features of complex fluid flows.

Wednesday 6:30 Woodway Foyer

GR10

### **Oscillating shear bands in a thixotropic yield-stress fluid**

Yufei Wei, Michael J. Solomon, and Ronald G. Larson

*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States*

We measure the local velocimetry in a thixotropic fumed silica suspension undergoing a shearing deformation with a constant apparent shear rate. This image shows the temporal evolution of the velocity profile (x-axis, time; y-axis, normalized position along the velocity gradient direction);

colormap, normalized velocity). The initially uniform flow gradually separates into bands with different local shear rates. The shear bands exhibit sustained periodic oscillations along with slow and irregular evolutions.

Wednesday 6:30 Woodway Foyer

GR11

### **Stability of viscous fingering patterns in colloidal gels**

Irmgard Bischofberger<sup>1</sup>, Badis Marsit<sup>1</sup>, Yacouba Kaloga<sup>2</sup>, and Thibaut Divoux<sup>2</sup>

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Pattern formation in fluids are involved in numerous physical process in which mechanical mixing, chemical reactions, evaporation and/or surface effects play a key role. In the case the pattern develops in a non-Newtonian fluid, the non-linear rheology interferes with the patterning process, which often generates a richer dynamics than the one commonly observed for a Newtonian fluid. Here we focus on the viscous fingering instability in a time-dependent yield stress fluid. We study experimentally the flow of a carbon black gel sandwiched in a parallel plate geometry, for which the upper plate is being lifted up at constant velocity. We show the existence of a critical lift velocity, above which the flow becomes unstable, yielding to the growth of viscous finger originating from the Saffman-Taylor instability at the fluid-air interface. The resulting pattern in the gel consists in a tree-like branched structure, and covers only a fraction of the plate surface. Varying the gel concentration, we demonstrate that the extent of the pattern is governed by the yield strain of the carbon black gel, while for a fixed gel concentration, the span of the pattern increases for increasing lift velocity and decreasing initial gap width. Finally, we show that the shear history of the gel has a strong influence on the pattern morphology and allows us to generate a broad variety of figures, from heavily ramified patterns composed of thin branches when the gel is rejuvenated by a preshear of high intensity followed by an abrupt flow cessation, to a coarse pattern characterized by a large core and fewer thick branches, when the gel is rejuvenated by a preshear of high intensity followed by a slow cessation of shear.

Wednesday 6:30 Woodway Foyer

GR12

### **Planar cholesteric liquid crystal flowers**

Virginia A. Davis<sup>1</sup> and Saha Partha<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Auburn University, Auburn, AL, United States;* <sup>2</sup>*Auburn University, Auburn University, AL 36849, United States*

Aqueous cholesteric dispersions of cellulose nanocrystals can form planar domains that give rise to selective reflection of light. However, achieving solid films domains with consistent saturation colors requires controlling the helix packing and alignment during drying. This work showed how the combination of concentration, orbital shear, and speed of drying could be used to achieve large domains with controlled morphology and optical properties.

Wednesday 6:30 Woodway Foyer

GR13

### **Band formation during post-shear relaxation in a biphasic aqueous sulfonated cellulose nanocrystal dispersion**

Matthew M. Noor and Virginia A. Davis

*Chemical Engineering, Auburn University, Auburn, AL, United States*

There is significant interest in producing macroscale materials with anisotropic optical, mechanical, or electrical properties via the controlled fluid phase assembly of rod-like nanomaterials. However, there is still relatively limited understanding of these systems' phase behavior, rheological properties and microstructural relaxation after shear cessation. In this study, rheology and rheo-optics were used to understand the behavior of the aqueous lyotropic system, sulfonated cellulose nanocrystals (CNC). Understanding post-shear relaxation is critical to understanding properties of solidified materials.

Wednesday 6:30 Woodway Foyer

GR14

### **Carbon nanotube macrostructures from controlled elongational flow**

Crystal E. Owens, A. John Hart, and Gareth H. McKinley

*Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

In these 3D-printed structures, more than 50 billion carbon nanotubes have assembled to form a delicate, conductive object. The sharp upper tip was created by necking due to capillary forces while printing in a mostly-extensional flow, reminiscent of the process which creates chocolate Hershey's Kisses. The scanning electron micrographs show a surface wrinkled by counterdiffusion and the evaporation-driven shrinkage from when the nanotubes precipitated from the original solvent and dried. At a closer scale, the alignment of large fibrils of nanotubes is evident, and the resulting high inter-tube contact area gives rise to the desirable conductivity of the structures.

Wednesday 6:30 Woodway Foyer GR15

### **Direct measurement of polymer chain alignment via time-resolved in-situ extensional rheo-SANS**

Carlos López-Barrón

*Exxon Mobil Chemical Company, Baytown, TX, United States*

This illustration shows a new technique based on in-situ SANS measurements which allows simultaneous measurements of stress and chain stretching during uniaxial extension of polymer melts. In addition, new time-resolved collection data protocols available in some neutron facilities allows structural measurements in very early stages of flow and during relaxation.

Wednesday 6:30 Woodway Foyer GR16

### **Shear thinning around a vibrating wire**

Cameron C. Hopkins and John R. de Bruyn

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Fluid flow past a cylinder has been studied extensively both numerically and experimentally, but the problem of a cylinder vibrating in a fluid that is initially at rest has received little attention. We have numerically studied the resonant behaviour of a cylinder vibrating in Newtonian fluids and in shear-thinning fluids described by the Carreau model. These visually captivating images show the complex spatial variation of the velocity, shear rate, and viscosity that results from small-amplitude vibrations of a cylinder in a shear-thinning fluid.

Wednesday 6:30 Woodway Foyer GR17

### **Foam rheology with viscoelastic surfactant solutions examined in microfluidic devices**

Eric D. Vavra, Leilei Zhang, and Sibani Lisa Biswal

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Switchable surfactants are amphiphilic chemical species that can be tuned in response to external stimuli such as temperature, pH, and light. These stimuli-responsive surfactants have numerous applications including foams for oil recovery, food production, drug delivery and detergency. More recently, switchable surfactants have been demonstrated to have excellent chemical and thermal stability for applications requiring high temperatures or salinities. The surfactant N,N,N'-trimethyl-N'-tallow-1,3-diaminopropane (TTM) is an example of such a switchable surfactant. TTM is uncharged at high pH values but switches to a cationic surfactant at low pH values due to protonation of the tertiary amine group.

We are exploring the rheology of foam this surfactant and how salinity, concentration, pH, and temperature all affect the flow of foaming TTM solutions in a microfluidic device. We are able to visualize the rheological traits of each surfactant solution including shear thinning and shear banding, which indicates the formation of worm-like micelles (WLMS). At static and very low shear conditions, a 2% TTM solution exhibits very viscous, solid-like behavior, where bubbles are entangled within an entangled micelle network. Upon increasing shear rate, the micelles disentangle and align with the flow resulting in shear-induced phase separation. Gas bubbles in the mobile phase travel quickly through the device while those in the trapped phase remain in the flow channel.

This image depicts a visual investigation of the shear-induced phase separation of TTM in a microfluidic device. Fluorescence and birefringence imaging techniques are employed to study the phase-separation behavior of a flowing TTM solution.

Wednesday 6:30 Woodway Foyer GR18

### **3D printing glass from colloidal suspensions**

Nikola Dudukovic, Jacob Long, Brian Chavez, James Wickboldt, and Rebecca Dylla-Spears

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Nikola Dudukovic and co-workers produce transparent glass with spatial change in refractive index by 3D printing suspensions (inks) of silica nanoparticles and a titania precursor dopant. A predictive methodology is developed to allow formulation of inks with targeted rheology and matching solids concentrations for multimaterial 3D printing. This presents a vital step towards additive manufacturing of functionally designed optical components. \*This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program (16-SI-0003). LLNL-PHOTO-756554.\*

Wednesday 6:30 Woodway Foyer GR19

### **Bread dough: A polymer network you can see, feel, and eat**

R. E. Corman, Tristan Antonsen, and Randy H. Ewoldt

*Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Gluten is the main protein in wheat-based bread doughs. The presence of these proteins is responsible for the viscoelastic rheologically-complex nature of bread dough, include its characteristic power-law relaxation. Working with bread dough gives the baker a hands-on experience of seeing and feeling these complex network structures and their resulting rheological characteristics. These networks, influenced by flour type, rising time, and processing is integral in the rise, gas retention, and quality of the final loaf.

Wednesday 6:30 Woodway Foyer

GR20

**Control over distribution of pores in the polymer films fabricated via evaporation induced phase separation**Rumiya Pervin*Chemical Engineering Department, Indian Institute of Technology, Chennai, Tamilnadu 600036, India*

Abstract Evaporation induced phase separation (EIPS) is a simple and versatile technique for the fabrication of macrostructured polymer films. In this technique, the polymer films are fabricated by drying a homogeneous solution of three components i.e., polymer/solvent/non-solvent mixture. By considering a mixture of poly (methyl methacrylate)- tetrahydrofuran- water (PMMA- THF- H<sub>2</sub>O), we report a rational approach to tune the distribution of pores in the polymer films formed via EIPS. The solvent and the non-solvent evaporate during the film formation, and therefore the drying induced composition and microstructural changes dictate the ultimate polymer film morphology. In this work, the temporal evolution of the microstructure, the phase behavior and the composition change path in relation to the isothermal ternary phase diagram of PMMA- THF- H<sub>2</sub>O during drying is monitored to provide insights into the origin of pore distribution in the final polymer films. The thermodynamic liquid-liquid phase separation can be comprehended by plotting composition paths on the ternary phase diagram. We show that by changing the initial concentration of water and PMMA in the casting solution and also by changing the initial thickness of the casting solution, polymer films of different morphology can be designed which includes - 1) non porous i. e., dense film 2) porous film with uniform pores distributed throughout the film thickness 3) composite film or asymmetric film i.e., nonporous top layer supported by porous sub layers.

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Wednesday 6:30 Woodway Foyer

GR21

**Mechanical contour mapping of human blood**Tyler Helton<sup>1</sup>, Matthew J. Armstrong<sup>2</sup>, and Jeffrey S. Horner<sup>3</sup>

<sup>1</sup>*Medical School, USUHS, Bethesda, MD 20814, United States;* <sup>2</sup>*Chemistry and Life Science, United States Military Academy, West Point, NY 10996, United States;* <sup>3</sup>*Chemical and Biomolecular Engineering, University of Delaware, Newark, DE, United States*

Human blood is an excellent example of a shear-thinning, thixo-elasto-visco-plastic material. An underdeveloped area of study is analyzing mechanical properties of blood for use in clinical diagnoses, particularly in analysis of transient data. There is a possibility that blood could be classified using its own unique transient mechanical signature, and with the addition of large quantities of data could be used as a method of diagnoses and/or differentiation. In this work, the use of a transient shear flow experiment called a triangle ramp experiment is utilized as a method of producing a mechanical contour mapping of blood. Hysteresis tests alleviate some of the nonlinear difficulties exhibited by LAOS. Rather than using the traditional discrete Fourier transform to analyze the data, a recent method, called Series of Physical Processes (SPP), is applied to the hysteresis curves<sup>1,2</sup>. SPP allows the visualization of the evolving viscous and elastic nature of the material, with the understanding the microstructure or thixotropic nature of the blood can contribute to both via stretching, and adding to the resistance to flow.





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## Plenary Lectures and Award Presentation

- Monday, October 15**  
8:30 AM  
Galleria I  
**Shear thickening in the real world: The application of suspension rheology to industrial processes**  
Wilson Poon  
*School of Physics and Astronomy, The University of Edinburgh*
- Tuesday, October 16**  
Bingham Lecture, 8:30 AM  
Galleria I  
**Rheology of ring polymer melts**  
Michael Rubinstein  
*Mechanical Engineering and Materials Science, Duke University*
- Wednesday, October 17**  
8:30 AM  
Galleria I  
**Connecting rheology to nanoscale structure of block copolymer micelle liquid crystals and nanocomposites**  
Lynn M. Walker  
*Chemical Engineering, Carnegie Mellon University*
- Thursday, October 18**  
Metzner Award Presentation  
8:00 AM, Galleria I  
**Memory effects in colloidal gels**  
Thibaut Divoux  
*MSE<sup>2</sup>, CNRS Bordeaux, CNRS-MIT*

## Social Program and Special Events

- Sunday, October 14**  
**SoR Outreach Event**  
1:00 PM – 4:00 PM                      Children's Museum of Houston  
**Welcoming Reception**  
6:30 PM – 8:30 PM                      Monarch Room  
*Reception sponsored by TA Instruments*
- Monday, October 15**  
**Student-Industry Forum**  
12:00 PM – 1:15 PM                      Monarch Room  
*Sponsored by American Institute of Physics and The Dow Chemical Company*  
**Gallery of Rheology Preview**  
1:30 PM – 4:00 PM                      Galleria Foyer  
**Monday Evening Reception**  
6:30 PM – 9:30 PM                      Saint Arnold Brewing Company
- Tuesday, October 16**  
**Gallery of Rheology Preview**  
8:30 AM – 4:00 PM                      Galleria Foyer  
**Society Business Meeting**  
12:00 PM – 1:30 PM                      Galleria Ballroom I  
**Awards Reception**  
7:00 PM – 8:00 PM                      Galleria Foyer  
**Awards Banquet**  
8:00 PM                                      Monarch Room
- Wednesday, October 17**  
**Gallery of Rheology Preview**  
8:30 AM – 4:00 PM                      Galleria Foyer  
**Poster Session and Reception**  
6:30 PM – 8:30 PM                      Woodway II & III Ballrooms  
*Reception sponsored by Anton-Paar USA*  
**Gallery of Rheology Contest**  
6:30 PM – 8:30 PM                      Woodway Foyer  
Online voting 10 AM – 8 PM

*The Society of Rheology gratefully acknowledges the generous support of TA Instruments, Anton-Paar USA, Malvern Panalytical, American Institute of Physics, The Dow Chemical Company, National Institute of Standards and Technology, and Halliburton.*