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THE SOCIETY OF RHEOLOGY

83^{RD} ANNUAL MEETING
PROGRAM AND ABSTRACTS

InterContinental Cleveland
Cleveland, Ohio
October 9 - 13, 2011

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Meeting Schedule

Monday, October 10, 2011

	AMA	*AMB*	*FBA*	*FBB*	*R204*	*R207*
8:30	J. J. de Pablo (PL1) - *AM*					
9:20	Coffee Break					
10:00	BS1	SC1	SI1	MB1	MF1	IR1
10:25	BS2	SC2	SI2	MB2	MF2	IR2
10:50	BS3	SC3	SI3	MB3	MF3	IR3
11:15	BS4	SC4	SI4	MB4	MF4	IR4
11:40	BS5	SC5	SI5	MB5	MF5	IR5
12:05	Lunch Break / Society Business Meeting					
1:30	BS6	SC6	SI6	MB6	MF6	IR6
1:55	BS7	SC7	SI7	MB7	MF7	IR7
2:20	BS8	SC8	SI8	MB8	MF8	IR8
2:45	BS9	SC9	SI9	MB9	MF9	IR9
3:10	Coffee Break					
3:35	BS10	SC10	SI10	MB10	MF10	IR10
4:00	BS11	SC11	SI11	MB11	MF11	IR11
4:25	BS12	SC12	SI12	MB12	MF12	IR12
4:50	BS13	SC13	SI13	MB13	MF13	IR13
5:15	BS14	SC14	SI14	MB14	MF14	IR14
5:40	End					
6:30	Society Reception					

Tuesday, October 11, 2011

	AMA	*AMB*	*FBA*	*FBB*	*R204*	*R207*
8:30	E. S. Shaqfeh (PL2) - *AM*					
9:20	Coffee Break					
10:00	SG1	SC15			MF15	CR1
10:25	SG2	SC16			MF16	CR2
10:50	SG3	SC17			MF17	CR3
11:15	SG4	SC18			MF18	CR4
11:50	SG5	SC19			MF19	CR5
12:05	Lunch Break					
1:30	SG6	SC20	FS1	MB15	MF20	CR6
1:55	SG7	SC21	FS2	MB16	MF21	CR7
2:20	SG8	SC22	FS3	MB17	MF22	CR8
2:45	SG9	SC23	FS4	MB18	MF23	CR9
3:10	Coffee Break					
3:35	SG10	SC24	FS5	MB19	SA1	CR10
4:00	SG11	SC25	FS6	MB20	SA2	CR11
4:25	SG12	SC26	FS7	MB21	SA3	CR12
4:50	SG13	SC27	FS8	MB22	SA4	CR13
5:15	SG14	SC28	FS9	MB23	SA5	CR14
5:40	End					
7:00	Awards Reception					
8:00	Awards Banquet					

Wednesday, October 12, 2011

	AMA	*AMB*	*FBA*	*FBB*	*R204*	*R207*
8:30	D. J. Pine (PL3) - *AM*					
9:20	Coffee Break					
10:00	SG15	SC29	FS10	MB24	SA6	PS1
10:25	SG16	SC30	FS11	MB25	SA7	PS2
10:50	SG17	SC31	FS12	MB26	SA8	PS3
11:15	SG18	SC32	FS13	MB27	SA9	PS4
11:40	SG19	SC33	FS14	MB28	SA10	PS5
12:05	Lunch Break					
1:30	SG20	SC34	FS15	MB29	SA11	PS6
1:55	SG21	SC35	FS16	MB30	SA12	PS7
2:20	SG22	SC36	FS17	MB31	SA13	PS8
2:45	SG23	SC37	FS18	MB32	SA14	PS9
3:10	Coffee Break					
3:35	SG24	SC38	FS19	MB33	SA15	PS10
4:00	SG25	SC39	FS20	MB34	SA16	PS11
4:25	SG26	SC40	FS21	MB35	SA17	PS12
4:50	SG27	SC41	FS22	MB36	SA18	PS13
5:15	End					
5:30	Poster Session & Reception					

Thursday, October 13, 2011

	AMB	*R207*	*FBA*	*FBB*	*R204*
8:00	R. S. Graham (AP1) - *AMB*				
8:40	SG28	SC42	FS23	MB37	SA19
9:05	SG29	SC43	FS24	MB38	SA20
9:30	SG30	SC44	FS25		SA21
9:55	Coffee Break				
10:25	SG31	SC45	FS26	MB40	SA22
10:50	SG32	SC46	FS27	MB41	SA23
11:15	SG33	SC47	FS28	MB42	SA24
11:40	SG34	SC48	FS29	MB43	SA25
12:05		SC49	FS30	MB44	SA26
12:30	End				

Session and Room Codes

AP = Award Presentations
BS = Rheology in Biological Systems
CR = Computational Rheology
FS = Non-Newtonian Flows and Stability
IR = Industrial Rheology
MB = Rheology of Polymer Melts and Blends
MF = Microfluidics, Microrheology and Confined Systems

PL = Plenary Lectures
PS = Polymer Solution Rheology
SA = Self-Assembling, Associative and Gel-like Systems
SC = Suspensions, Colloids and Emulsions
SG = Rheology of Solids, Glasses and Composites
SI = Surface and Interfacial Rheology

AM = Amphitheater A/B
AMA = Amphitheater A
AMB = Amphitheater B
FB = Founders Ballroom
FBA = Founders Ballroom A
FBB = Founders Ballroom B
R204 = Room 204
R207 = Room 207

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Monday Morning

Symposium PL

Plenary Lectures

Monday 8:30 Amphitheater A/B PL1

Directed assembly of complex fluids, and its application to nanoscale fabrication

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There is considerable interest in devising fabrication strategies that rely on the inherent ability of certain complex fluids and materials to self assemble into ordered structures having characteristic dimensions in the nanoscale. Over the past several years our research group has sought to develop strategies to drive and direct that self assembly by relying on multi-scale modeling. Depending on the system and issues of interest, the relevant models and methods can vary considerably in nature and level of resolution, ranging from fully atomistic to highly coarse grained; in this presentation I will provide an overview of various modeling approaches, along with a discussion of their usefulness and limitations, in the context of two distinct nanofabrication platforms.

The first is concerned with the formation of ordered, defect-free block copolymer structures in thin films. Recent work has shown that block polymer lithography offers considerable promise for large-scale production of next-generation electronic devices. A new mesoscopic formalism has been developed to describe the structure and dynamics of block copolymer blends and composites, and we use it to understand the role of surfaces and different types of directed-assembly strategies on the free energy (and the concomitant stability) of a variety of morphologies of interest for lithographic fabrication. Our models suggest that many of these structures represent non-equilibrium states that are accessed by specific processing routes, and simulations can be used to discern the boundaries between such states and stable, equilibrium morphologies.

The second application is concerned with the development of liquid-crystal based sensors. A multiscale model has been used to design liquid-crystal based devices for detection of biological molecules or toxins. In one implementation, liquid crystals are used to drive the assembly of nanoscale particles into highly regular structures, including chains, upon exposure to specific chemicals. In a different implementation, liquid crystal nanodroplets are shown to adopt distinct configurations upon exposure to specific analytes. As discussed in this presentation, multiscale models can be used to explain the origin and magnitude of the liquid-crystal mediated forces that arise between particles, and to interpret the nature of ordered morphologies that arise in laboratory experiments on droplets, thereby providing general design principles for rational development of effective sensing devices.

Symposium BS

Rheology in Biological Systems

Organizers: Patrick Underhill and Alejandro G. Marangoni

Monday 10:00 Amphitheater A BS1

Can we make rheology easier to swallow? Pt II – the ‘pharyngial squeeze’

Adam S. Burbidge and Jan Engmann
Nestec SA, Lausanne, Vaud, Switzerland

The swallowing process is an intricately synchronized and surprisingly robust sequence of bio-physical motions coupled with flows of food bolus (fluid) and air. However, when things do go wrong the consequences can range from slight choking, which is unpleasant, through to severe aspiration, which is a significant factor in the development of pneumonia. There is therefore a considerable motivation to better understand the biomechanics of the swallowing process in the hope of mitigating any such problems. It seems that swallowing of fluids generally proceeds in two phases. Firstly, the tongue acts in a manner similar to a peristaltic pump, and generates a high Reynolds number flow, forcing the majority of material quickly through the pharynx, the "upper esophageal sphincter" and finally into the esophagus. However, after this initial flow, there is a residual boundary layer of material, which 'coats' the pharynx. This residual material is generally swept out in the second phase of the swallowing process (another type of peristaltic squeezing between the back of the tongue and the pharynx). We discuss the fluid mechanics of this 'pharyngeal squeeze' and how it may be affected by different types of fluid rheology.

Monday 10:25 Amphitheater A BS2

A volume-expanding self-defense gel: The non-linear rheology of hagfish slime

Randy H. Ewoldt[1], Timothy M. Winegard[2], Douglas S. Fudge[2], and Gareth H. McKinley[3]
[1]Institute for Mathematics and its Applications, University of Minnesota, Minneapolis, MN 55455-0134, United States; [2]Department of Integrative Biology, University of Guelph, Guelph, Ontario N1G 2W1, Canada; [3]Massachusetts Institute of Technology, Cambridge, MA 02139, United States

We report the first experimental measurements of nonlinear rheological material properties of hagfish slime, a hydrated biopolymer/biofiber gel network, and develop a microstructural constitutive model to explain the observed nonlinear viscoelastic behavior. The linear elastic modulus of the network is observed to be G' ~ 2 Pa for timescales of 0.1s to 10s, making it one of the softest elastic biomaterials known. Nonlinear rheology is examined via simple shear deformation, and we observe a secant elastic modulus which strain-softens at large input strain while the local tangent elastic modulus strain-stiffens simultaneously. This juxtaposition of simultaneous softening and stiffening suggests a general network structure composed of nonlinear elastic strain-stiffening elements, here modeled as Finite Extensible Nonlinear Elastic (FENE) springs, in which network connections are destroyed as elements are stretched. We simulate the network model in oscillatory shear and creep, including instrument effects which cause inertio-elastic creep ringing. The network model captures the simultaneous softening of the secant modulus and stiffening of tangent modulus as the model enters the nonlinear viscoelastic regime.

Monday 10:50 Amphitheater A BS3

Methodology for rigorous rheological characterization of biological hydrogels

Christopher J. Rivet[1], Jonathan M. Zuidema[1], Faith A. Morrison[2], and Ryan J. Gilbert[1]
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Rheological characteristics of biological hydrogels are frequently assessed, but the assessment is often incomplete. Commonly, the battery of rheological tests employed is minimal with the purpose of comparing different biological hydrogels to the native tissue the hydrogels are designed to replace. Since the thoroughness and the standardization of rheological testing for biological hydrogels is lacking, it is difficult to compare rheological data between studies. Here, we present methodology for the rigorous rheological characterization of five distinct biological hydrogels. Of these, Matrigel™, an extracellular matrix based composite, collagen, and methylcellulose solidify upon heating whereas agarose, a seaweed derived polysaccharide, solidifies upon cooling. Fibrin hydrogels solidify due to an enzymatic reaction. The first step to the procedure is to define the linear regime for both strain and frequency functions. Each hydrogel is fully gelled prior to beginning and then subjected to small amplitude oscillatory shearing. The sinusoidal function imposed on the material by the parallel plate geometry is first subjected to a range of strains (0.1 to 100%) while holding the frequency constant. From these results, a value for strain (~10%) is chosen from the linear regime of the elastic modulus. Next, the linear domain of the elastic modulus from a variable frequency test (0.01 to 100Hz), using 10% strain, is determined. These two tests may need to be repeated in an iterative cycle in order to ensure that the arbitrarily chosen, initial values are correct. The final test applies the acquired strain and frequency values (10%, 1Hz) to the hydrogel in liquid phase and monitors the gelation profile as the temperature transitions to gelation point. These results display the final elastic and loss modulus as well as the rate of gelation, which are all critical parameters in biological applications. Creating a standardized characterization procedure permits direct comparisons between hydrogel platforms.

Monday 11:15 Amphitheater A BS4

Direct observation of flexible polymer chain relaxation using ssDNA

Christopher A. Brockman, Folarin B. Latinwo, and Charles M. Schroeder
Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, United States

We report the direct observation of chain relaxation for single flexible polymers at the molecular level. Recently, we developed a new experimental system for single molecule studies of flexible polymers based on single stranded DNA (ssDNA). We developed a biochemical synthesis platform for producing long strands of fluorescently-labeled ssDNA suitable for single polymer experiments. ssDNA molecules are synthesized to contain "designer" sequences, which avoids intrachain base pairing interactions. Using this system, we directly observe the relaxation process for single ssDNA polymer chains, thereby extending experimental studies of single polymer dynamics to a new class of molecules. Indeed, the vast majority of previous single polymer studies have relied on double stranded DNA, a semi-flexible polymer with markedly different molecular properties compared to flexible polymer chains (dsDNA persistence length ˜66 nm; ssDNA persistence length ˜0.6 nm). In this work, we present results from initial studies of ssDNA relaxation dynamics, which effectively highlights the differences in dynamics between "real" flexible polymers and "ideal" chains. We use fluorescence microscopy to characterize polymer chain relaxation from high stretch in free solution within a microfluidic device, and we present results for ssDNA chain relaxation as a function of polymer molecular weight and salt concentration. We compare results from single polymer experiments of chain relaxation to Brownian dynamics simulations incorporating force-extension elastic relations appropriate for flexible polymers. Using a combined experimental and computational approach, we explore the importance of backbone flexibility and solvent quality on chain relaxation, and we determine dynamical scaling laws for ssDNA chain relaxation. Overall, we seek a molecular-based understanding of the non-equilibrium dynamics of flexible polymer chains, which is crucial for control of polymer processing and molecular self-assembly.

Monday 11:40 Amphitheater A BS5

Relaxation pathway of a self-entangled DNA molecule back to a coil

Patrick S. Doyle and Jing Tang
Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Entanglements and knots continue to fascinate polymer physicists due to their biological relevance, rheological implications and general complexity. While many theoretical studies and some simulations have been performed to study the relaxation of a collapsed, entangled polymer globule back to a random coil, experimental data has been quite elusive. In this work we present single molecule experiments that allow us to follow the relaxation pathway of an initially self-entangled DNA molecule back to an equilibrium coil. Single molecule fluorescence microscopy experiments allow us to demonstrate that the pathway back to equilibrium involves passing through two different metastable arrested conformation states. Importantly, we show strong evidence of intramolecular entanglements and the existence of knots. We also show a new route in the pathway that involves an end mediated nucleation event. These results have broad importance in DNA separations and single molecule genomics, polymer rheology, and biomolecular nanotechnologies.

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Monday 10:00 Amphitheater B SC1

Modification of biomass rheology: The influence of physical chemistry

Joseph R. Samaniuk[1], C. T. Scott[2], Thatcher W. Root[1], and Daniel J. Klingenberg[1]
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Chemicals derived from lignocellulosic biomass, including liquid fuels, are a sustainable alternative to petroleum derivatives. Many different processes have been proposed to convert lignocellulosic materials to liquid fuels but a common operation required in all of them is heating to high temperatures (110-230^{o}C). Reducing the concentration of water during this step decreases utility costs and overall capital costs by reducing equipment size. Increasing the solids concentration however, results in rheological changes like a rapidly increasing yield stress. Mixing, pumping and pouring biomass slurries becomes difficult, if not impossible, above 20-30 wt% solids.

We have shown previously that the rheology of biomass can be controlled with the use of certain water soluble polymers (WSPs). Colloidal probe microscopy experiments have revealed that WSPs alter stresses in cellulose fiber suspensions by lubricating the surface of individual fibers. Using these additives, we have been able to mix and convey untreated biomass at solids concentrations up to 50 wt%. However, the efficacy of WSPs is reduced after certain treatments such as acid hydrolysis. How changes in the physical chemistry of biomass during treatment affect rheology modification with WSPs is unknown.

In this presentation our focus will be on the influence of the physical chemistry of both biomass and WSPs on rheological modification. The physical chemistry of the biomass is altered by the treatment type (e.g. acid hydrolysis) and the treatment severity. Specific changes to the physical chemistry of the biomass are probed with fiber suspensions containing known chemistries (e.g. cellulose fibers vs. hemicellulose-rich fibers). The physical chemistry of the WSPs are altered by varying the type of polymer, the molecular weight, the degree of substitution, and by the addition of chemical additives. We will show how these variables influence not only the instantaneous rheological modification but also its behavior over time.

Monday 10:25 Amphitheater B SC2

Activated relaxation, elasticity and yielding in dense suspensions of nonspherical colloids

Rui Zhang and Kenneth S. Schweizer
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Our microscopic theory of cooperative translation-rotation activated glassy dynamics of dense suspensions of hard uniaxial particles [PRE, 80, 011502 (2009); JCP,133,104902 (2010)] is extended to treat nonlinear viscoelasticity and the consequences of short range attractions. Under quiescent conditions, a plastic glass (PG) state exists for weak attractions and small aspect ratio dicolloids, but is destroyed beyond a critical attraction strength resulting in a new dynamic triple point (fluid, PG, gel), and two novel re-entrant behaviors: PG-fluid-gel, and repulsive glass(RG)-PG-gel. A qualitatively new mixed "glass-gel" state also emerges at intermediate attraction strengths. At very high volume fractions, increasing attraction transforms the RG to an attractive glass (AG) characterized by a dynamic free energy surface with gel-like localization but a glass-like transition state. AG dynamics is of a two-step nature where physical bonds first break followed by hopping over a glass-like barrier, and the structural relaxation time becomes a strongly non-monotonic function of attraction strength. At high enough attraction strength a sharp crossover from a gel to AG with increasing volume fraction is predicted. As the particle aspect ratio grows, the PG state is destroyed, and translational motion becomes increasingly more important for escaping kinetic traps. The behavior of chemically heterogeneous Janus dicolloids have also been studied, with distinct differences emerging due to physical clustering. Stress-induced two-step dynamic yielding is predicted for dicolloids of modest aspect ratios, in accord with the recent experiments of Kramb and Zukoski. Its physical origin is the presence of two activation barriers in the dynamic free energy under quiescent conditions, where stress first liquidfies the softer rotational degree of freedom followed by the center-of-mass translation. A crossover to one-step yielding is predicted when the rotational and translational dynamics becomes highly coupled.

Monday 10:50 Amphitheater B SC3

Yield stress of biomass suspensions using magnetic resonance imaging

David M. Lavenson[1], Emilio J. Tozzi[1], Michael J. McCarthy[2], and Robert L. Powell[1]

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Cellulose fibers in water form networks that give rise to an apparent yield stress, especially at high solids contents. Measuring the yield stress and correlating it with fiber mass concentration is important for the biomass and pulp industries. Understanding how the yield stress behaves at high solids concentrations is critical to optimizing the enzymatic hydrolysis of biomass in the production of biofuels. Rheological studies on pretreated corn stover and various cellulosic fibers have shown that yield stress values correlate with fiber mass concentration through a power-law relationship. We use magnetic resonance imaging (MRI) as an in-line rheometer to measure velocity profiles during pipe flow. If coupled with pressure drop measurements, these allow yield stress values to be determined. We found that, when compared with literature values based on conventional off-line rheometers, our results were accurate and followed the power-law relationship. In addition, the rheo-MRI method has measurement uncertainties that compare favorably with conventional techniques. A main factor that contributes to low uncertainties is the capability to process larger samples. Some distinctive features of the technique are short sampling times, and the direct visualization of the unyielded region in the velocity profiles. Length scale effects that arise in conventional rheometers due to small ratios between gap and particle length are avoided by employing pipe diameters much larger than the particle size.

Monday 11:15 Amphitheater B SC4

The rheology of nanofibrillated cellulose (NFC) suspensions

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Nanofibrillated cellulose (NFC) is a renewable material that has the potential to obtain unique material properties for many end products. NFC used in this study was prepared mechanically with a pilot scale refiner starting with bleached softwood kraft fibers. The suspensions obtained are 3.5% solid which was increased up 13.5% using a filtration process. The rheology of this suspension was measured by control shear rheometer in which the steady shear viscosity and oscillatory shear test were used to characterize the flow properties of the suspension. Two geometries of cone and plate and parallel plate were compared. Steady shear viscosity measurements are difficult because the material seems to slip from contact with the surfaces and can be ejected from the rheometer gap. This behavior is similar to that reported by Stickel et al. (2009). Oscillatory shear tests, however, give consistent results. NFC is a highly shear thinning material with a power law index of around 0.1. As expected, higher solids increased the viscosity at all shear rates, but the general shear thinning behavior was not changed. The complex viscosity, storage and loss moduli, and the yield stresses are reported for a range of solids.

Stickel J.J, J.S. Knutsen, M. Liberatore, W. Luu, D.W. Bousfield, D.J. Klingenberg, C. T. Scott, T. Root, M. Ehrhrdt, and T. Monz, "Rheology Measurements of a Biomass Slurry, An Interlaboratory Study", Rheology Acta, 48(9): 1005-1015 (2009).

Monday 11:40 Amphitheater B SC5

Intrinsic viscosity of actively swimming microalgae suspensions

Randy H. Ewoldt[1], Lucas M. Caretta[2], Ahammed Anwar Chengala[3], and Jian Sheng[4]

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Suspensions of actively swimming microorganisms exhibit an effective viscosity which may depend on volume fraction, cell shape, and the nature of locomotion (e.g. "pushers" vs. "pullers"). Although several dilute-regime theories have been offered for active suspensions, no experimental study to our knowledge has been able to resolve the dilute-regime intrinsic viscosity of actively swimming microorganism suspensions. Here we use a cone-and-plate rheometer to experimentally measure the dynamic shear viscosity for motile and non-motile suspensions of unicellular green algae (Dunaliella primolecta, a biflagellated "puller"). The low viscosity biological samples require careful experimental protocols to avoid settling, to avoid flow-induced migration, and to minimize precision error. With these protocols in place we can distinguish the intrinsic viscosity which we show is higher for the motile "puller" swimmers compared to the immobilized counterparts. This observation is consistent with recently proposed dilute-regime theories which predict that "pullers" should have a higher viscosity than non-motile suspensions.

Symposium SI

Surface and Interfacial Rheology

Organizers: Jan Vermant and Eric Weeks

Monday 10:00 Founders Ballroom A SI1

A new droplet-based method for compressible and incompressible interfacial rheology

Kendra A. Erk[1], Frederick R. Phelan Jr.[1], Steven D. Hudson[1], Jonathan T. Schwalbe[2], and Jeffrey D. Martin[3]
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Droplet deformation and rupture, emulsion viscoelasticity, coalescence - nearly all of the properties and performance of emulsions - are governed and influenced by interfacial rheology. Generally, different techniques are required to measure either interfacial shear or dilatational properties. Here, we describe a new technique that measures both properties directly from the dynamics of surfactant-stabilized droplet interfaces. We determine the shear and dilatational viscosities of the interface by measuring the velocity at selected locations in the droplet and inputting these velocities into a recently developed analytical model. We find that the shear viscosity of the interface populated by block copolymer surfactant is greater than with small molecule alcohol surfactant. The apparent dilatational viscosity is generally much larger than the interfacial shear viscosity, and possible elastic effects are discussed. Investigation of small droplets is of interest not only for their relevance to emulsion applications, but their small size has potential for improved force sensitivity and temporal resolution.

Monday 10:25 Founders Ballroom A SI2

Analysis of the flow profiles in the interfacial shear magnetic rod rheometer

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Several technological applications, consumer products and biological systems derive their functioning from the presence of a complex fluid interface with visco-elastic rheological properties. The intimate coupling of the bulk complicates measurements of the rheological properties of such an interface and interfacial flows complicate the analysis. In the present work, analytical, numerical and experimental results of the interfacial flow fields in a magnetic rod interfacial Stress Rheometer (ISR) will be presented. Mathematical solutions are required to correct the experimentally determined apparent interfacial shear moduli and phase angles for the drag exerted by the surrounding phases, especially at low Boussinesq numbers. Starting from the Navier-Stokes equations and using the generalized Boussinesq-Scriven equation as a suitable boundary condition, the problem is solved both analytically and numerically. In addition, experimental data of the interfacial flow field are reported, obtained by following the trajectories of tracer particles at the interface with time. Good agreement is found between the three methods, indicating that both the analytical solution and the numerical simulations give an adequate description of the flow field and the local interfacial shear rate at the rod. Based on these results, an algorithm to correct the data of the ISR is proposed and evaluated, which can be extended to different geometries. An increased accuracy is obtained and the measurement range of the ISR is expanded towards viscosities and elastic moduli of smaller magnitude. Result for simple fatty acids and particle laden interfaces will be presented.

Monday 10:50 Founders Ballroom A SI3

Interfacial viscoelasticity, yielding and creep ringing of globular protein-surfactant mixtures

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Serum albumins play a vital role in various biological processes in mammalian blood. Even at low concentrations, Bovine Serum Albumin (BSA) solutions exhibit an apparent yield stress in bulk rheological measurements. Interfacial steady shear and small amplitude oscillatory shear measurements are performed using the double wall ring (DWR) fixture attached to a stress-controlled rheometer, and these results are compared with measurements of the bulk viscosity using an interface-free microfluidic rheometer. The results show that interfacial viscoelasticity leads to the appearance of an apparent yield stress and strong shear thinning in the effective viscosity of the solutions. We show that the interfacial contribution is well captured using a simple Bingham-like additive model. The distinctive oscillatory response that arises from the coupling between instrument inertia and sample elasticity in creep experiments with the DWR is also exploited to make surface viscoelasticity measurements. Interfacial viscoelastic storage and loss moduli are extracted directly from the observed oscillations as well as from a linear Jeffreys model fitted to the damped oscillatory response seen at small strains. We show that the interfacial response rapidly becomes non-linear at higher strains, and is well modeled using a non-linear model with fractional elements. We also use these techniques to study the systematic changes in the interface rheology that take place upon the addition of a non-ionic surfactant, Tween 80, and show that the surface elasticity progressively decreases with increasing surfactant concentration. We find that a steep change in surface elasticity takes place at a bulk surfactant concentration close to the critical micelle concentration. Competition between the surfactant and BSA for adsorption at the interface leads to the progressive displacement of the protein from the interface and this results in elimination of the viscoelastic ringing response beyond a critical bulk surfactant concentration.

Monday 11:15 Founders Ballroom A SI4

Microrheology of phospholipid monolayers at the air-water interface

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We report systematic measurements of the rheological properties of phospholipid monolayers at an air-water interface. Using microfabricated, ferromagnetic microbuttons as new rheological probes, we have measured both the linear and nonlinear viscoelastic responses of phospholipid monolayers as a function of both surface pressure and frequency. Visualization of the interfacial monolayers using fluorescence microscopy revealed that the interlocked, spiral liquid crystalline domains give rise to a viscoelastic solid response, analogous to a two-dimensional emulsion. The measured viscoelastic moduli qualitatively agreed with predictions based on a two-dimensional concentrated emulsion model. In addition, small amounts of cholesterol added to the phospholipids dramatically changed the domain structure as well as rheological responses of the monolayers. The observed rheological phenomena have important implications for replacement human lung surfactants in which the role of cholesterol remains hotly debated.

Monday 11:40 Founders Ballroom A SI5

Phases and phase transitions of a phosphatidylethanolamine monolayer studied by interfacial active microrheology

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The reorientation of a magnetic Nickel nanorod was used to study the surface viscosity of a DiMyristoyl PhosphatidylEthanolamine (DMPE) monolayer at the air-water interface. Surface viscosity and surface pressure were measured as a function of the molecular area. Our results indicate that the surface viscosity undergoes a sudden order of magnitude change at the surface pressure corresponding to a phase transition from a liquid expanded (LE)-liquid condensed (LC) coexistence phase to a liquid condensed (LC) phase. On further increase of surface pressure, the change in surface viscosity is gradual within the LC region. Further, while no measurable elasticity is detected in the LC region, onset of elasticity is noted at the surface pressure corresponding to the LC-Solid(S) transition previously recorded using synchrotron X-ray scattering. This indicates that the solid phase in the monolayer is primarily elastic. The increased sensitivity of our measurements is primarily due to the nanometer dimensions of our probe. Therefore, we conclude that increased sensitivity of interfacial microrheology can be used as a useful tool to monitor changes in the lateral molecular organization in phospholipid films.

Symposium MB

Rheology of Polymer Melts and Blends

Organizers: Joao Maia and Avraam I. Isayev

Monday 10:00 Founders Ballroom B MB1

Stress maximum and steady extensional flow of branched polymer melts

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A stress maximum during start-up of kinematically steady extensional flow was reported by Meissner in 1985 for low density polyethylene (LDPE)[Meissner 1985]. Subsequently observations of a steady stress following a stress maximum was reported for two LDPE melts (Lupolen3020D and Lupolen1840D) [Rasmussen et al., 2005]. Steady stress following a stress maximum has also been reported for a model branched (Pompom) polystyrene of known architecture [Nielsen et al., 2006]. However the rheological significance of the stress maximum as well as the existence of steady flow conditions following the maximum is still a matter of some debate [Wang 2009].

We here report observations of stress in extensional flows observed in a Filament Stretching Rheometer (FSR) [Bach et al. 2003] and a Cross-Slot Extensional Rheometer (CSER) [Auhl et al. 2011]. The FSR describes the transient stress in start-up of kinematically steady flow, while the CER describes kinematically steady flow. The steady stress values measured by the FSR after the stress maximum compare favorably with the steady stress values observed in the CER thereby giving credence to both methods. To cast further light upon the rheological processes involved in the stress maximum we report measurements of stress relaxation and reverse flow before and after the stress maximum. The measurements reveal a loss of elasticity associated with the maximum.

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Monday 10:25 Founders Ballroom B MB2

Molecular weight and rate effects in uniaxial extension of polymer melts

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A previous PTV study of SBR melts [Macromolecules 42, 6261 (2009)] has indicated strong macroscopic motions after step shear, which suggest that the elastic yielding resulted in localized breakdown of the entanglement network. We carry out a systematic parallel study to determine how similar nonlinear responses may occur upon uniaxial extension of the entangled polymer melts. We will show whether the previously observed [Phys. Rev. Lett. 99, 237801 (2007)] specimen breakup after step extension can occur involving Hencky rate lower than the Rouse relaxation rate and can show up only after a period longer than the Rouse time.

Monday 10:50 Founders Ballroom B MB3

What and where is the strain hardening and softening

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It is commonly accepted today that some entangled polymer melts show "strain hardening" in uniaxial extension but only strain softening in simple shear. A famous example is LDPE, which was described as showing strain hardening in extension and softening in shear (Phys. Today, August 2008, p. 40). We demonstrate that true strain hardening in non-crystalline melts can only occur in the limit of finite chain extensibility, often leading to rupture. Much of strain hardening discussed in the literature on extensional rheology of polymeric liquids arises from a straightforward geometric compactification that has no other physical meaning. This geometric exaggeration of the true stress is greater when the sample resists more to yielding, i.e., when it can be stretched more before the extension ends in either non-uniform stretching (necking) or specimen failure. We found no true strain hardening for commercial LDPE. Moreover, in the nonlinear regime, LDPE specimen never reaches the point of fully developed flow state before it breaks up. The same is true for most linear melts as well. Thus, it is never really instructive and insightful to represent the mechanical response in terms of the Cauchy (true) stress.

Monday 11:15 Founders Ballroom B MB4

Microscopic theory of the dynamic tube confinement potential for entangled liquids of rigid macromolecules

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We present a first-principles theory of the slow quiescent dynamics of a solution of infinitely thin, non-rotating rods. As objects with trivial equilibrium structure, entanglement dynamics are determined solely by bond uncrossability and macromolecular connectivity. Our work builds on the theory of Szamel, which exactly enforces uncrossability at the two-rod level in conjunction with a self-consistent renormalization to account for many-particle effects. This approach predicts the emergence of tube localization and long-time reptative diffusion above a critical density, consistent with simulations and the Doi-Edwards asymptotic scaling laws. The dynamic confinement potential for lateral motion is constructed based on local equilibrium and nonlinear Langevin equation ideas. In contrast with the usual tube model, distinct anharmonicities are predicted that severely soften (but do not destroy) the transverse confining forces. The spatial nature of the confinement potential is analyzed in detail, and shown to quantitatively agree with recent experiments on entangled F-actin solutions that observe highly nongaussian features in the transverse displacement distribution (long exponential tails). The theory also allows for an investigation of the strong effect of orientational alignment on tube confinement and dynamics, as relevant to rods under strong flows or quiescent nematic liquid crystals. Finally, our approach is extended to other macromolecular architectures. For solutions of non-reptating rigid crosses we propose rare local density fluctuations on the polymer size scale control macroscopic transport and result in an exponential decay of the diffusion constant with density, in agreement with recent simulations. Inspired by primitive paths ideas, a mapping between the rigid macromolecules and flexible chains/stars is proposed. This allows ab initio predictions to be made for the tube diameter, critical degree of entanglement, and transport properties of chain polymer solutions and melts.

Monday 11:40 Founders Ballroom B MB5

Microscopic theory of nonlinear rheology, relaxation and yielding in entangled polymer liquids

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We have developed a first-principles theory of the entanglement dynamics of a solution of infinitely thin, non-rotating rods based solely on bond uncrossability and macromolecular connectivity. Tube localization, reptation, and the full dynamic confinement potential under quiescent (isotropic and oriented) conditions are predicted. The new self-consistent approach is extended to treat the consequences of external stress based on a mechanical work idea. In contrast to the standard tube model, the transverse confinement potential is highly anharmonic and becomes softer with increasing rod displacement, orientation and/or applied stress. As a consequence, the transverse localization length grows with stress (tube dilation), and deformation results in a finite entropic barrier for lateral motion and hence the possibility of dynamic yielding via an activated hopping process. Moreover, the transverse tube constraint is completely destroyed beyond a critical yield stress or strain. Application of these ideas to nonlinear step strain and creep experiments, and steady state shear thinning, have been carried out. The key physics is that with increasing deformation a competition emerges between reptation and a parallel non-reptative relaxation channel involving transverse entropic barrier hopping, which depends on degree of entanglement, polymer orientation, and the strain amplitude, applied stress or Weissenberg number. As a result, the entanglement network can be severely modified or destroyed for strong enough applied forces. Finally, a theory at the level of effective forces exerted on a tagged polymer by its surroundings is formulated and applied to the problem of force imbalance and yielding under startup continuous shear for both entangled rod solutions and flexible chain melts. Comparisons of the predicted yield stress and strain as a function of deformation rate with both the experiments and qualitative entanglement decohesion ideas of Shi-Qing Wang and coworkers will be presented.

Symposium MF

Microfluidics, Microrheology and Confined Systems

Organizers: Amy Shen and Pat Spicer

Monday 10:00 Room 204 MF1

Extensional flow of worm-like micellar solutions in a microfluidic cross-slot device

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High extension rate flows of complex fluids such as worm-like micellar surfactant solutions are encountered in a wide variety of applications, including enhanced oil recovery and ink-jet printing. We investigate the stagnation point extensional flow of worm-like micellar solutions consisting of cetyl pyridinium chloride (CPyCl) and sodium salicylate (NaSal) dissolved in aqueous sodium chloride (NaCl) solutions of various ionic strength. Extensional flow is generated using a microscale cross-slot geometry, which enables micro-particle image velocimetry (μ-PIV) and full-field birefringence microscopy to be coupled with macroscopic measurements of the bulk pressure drop across the contraction. In the case of Newtonian fluids, μ-PIV shows that the elongational kinematics in the cross-slot remain symmetric and stable up to moderate Reynolds number, Re ~ 20. In the absence of added NaCl, worm-like micellar solutions with high CPyCl:NaSal concentrations display a symmetric flow field only for low values of the strain rate, such that the strain rate $\leq 1/\lambda_m$ where λ_m is the Maxwell relaxation time determined by fitting cone-and-plate oscillatory shear data. In this stable flow regime the fluid displays a sharply-defined birefringent strand extending along the outflow streamline from the stagnation point and the apparent extensional viscosity can be estimated from the total pressure drop measured across the cross-slot channel. For moderate deformation rates the flow remains steady but becomes increasingly asymmetric as the flow rate increases, before eventually becoming time dependent. Solutions with low CPyCl concentrations (in the absence of added NaCl) do not exhibit asymmetric or time-dependent flows, even at very high strain rate. However, on increasing the ionic strength by the addition of 100 mM NaCl, these fluids not only display elastic flow instabilities in the cross-slot, but also form irreversible flow-induced gel structures.

Monday 10:25 Room 204 MF2

A study of flow-induced structure formation in wormlike micellar solutions using local micelle density measurements

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Wormlike micellar solutions exhibit a wide variety of phenomena, one of which is the formation of flow-induced gel-like structures. In some cases these structures are temporary and disintegrate upon cessation of the flow, in other cases these structures can be stable and very long-lived. Here, we present a series of experiments examining flow-induced structure formation in microfluidic flows of a micellar solution. Using the fluorescent dye Nile red, we are able to measure the local micelle concentration of the solution during flow. We examine purely extensional flows, purely shear flows, and mixed flows. We find that in extensional and mixed flows local concentration variations on the order of 25% are observed during flow, while in purely shear flows no measurable concentrations variations are observed. We also consider how these flow-induced micelle concentration variations are related to the formation of the flow-induced structures previously reported in the literature.

Monday 10:50 Room 204 MF3

Presentation of biomolecules for analysis: Nano-confined DNA dumbbells

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Through control of confinement and ionic environment, we have developed an efficient system for presentation of DNA molecules for optical mapping. Such a system relies on the formation of DNA dumbbells, where large segments of the molecules remain outside of nanoslits that are used to confine them.The ionic environment enable the molecules to adopt a fully stretched configuration, thereby facilitating analysis by optical means. A molecular model and Brownian dynamics simulations are used in order to study and analyze the behavior of the system. A self-consistent coarse-grained Langevin description of the polymer dynamics is adopted in which hydrodynamic effects are included through a Green's function formalism. The $O(N)$ General Geometry Ewald-like Method is used to calculate the confined Stokeslet. We found that the balance between electrostatic and hydrodynamic interactions is responsible for observed molecular presentations. We demonstrate that the so-called Odijk regime starts when the confinement is of the same order of magnitude as the persistence length of the molecule, in contrast to literature arguments that suggest otherwise.

Monday 11:15 Room 204 MF4

Transition to elastic turbulence in 4:1 microcontraction flow

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Turbulence is one of the most interesting phenomena in nature and one of the biggest challenges in fluidics. In case of Newtonian fluids, flows are likely to be turbulent at large Reynolds number. However, viscoelastic fluids such as polymer solutions show different behavior due to their nonlinear rheological properties. Flows of flexible long-chain polymer solutions can be turbulent even when Reynolds number is low, because elastic stress increases when polymer molecules are significantly stretched. In that case elasticity replaces inertia. There were several studies on this phenomenon. However, most of them were focused on Couette-Taylor flows and curvilinear flows, and elastic turbulence in contraction geometry has rarely been studied. In this study, flow patterns which were developed by elasticity were systematically investigated in microcontraction channel flow. As the elasticity of flows is elevated either by the property of a fluid or flow condition, flow pattern develops from Newtonian-like flow to elastic turbulent flow. Diverging flows and steady vortex growth region are observed in between. Just before elastic turbulence, oscillating vortex was found. When the flow falls in that region, it is neither steady nor turbulent, because vortices fluctuate periodically. With these results, we suggest a transition mechanism of highly elastic flows in contraction geometry.

Monday 11:40 Room 204 MF5

Comparing extensional viscosities of food biopolymers in aqueous solutions via capillary break-up and microchannel rheometry

Jan Engmann and Adam S. Burbidge
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Carbohydrate biopolymers are used in food, beverage and nutrition products to stabilize microstructures and to modify the textural properties of these products. The effects of these ingredients on shear viscosity are often quite well characterized, while there is still a relative scarcity of published data concerning their effects on extensional flow behaviour. We present data obtained by filament thinning and microchannel contraction flows for different biopolymers in aqueous solutions at different pH and ionic strength conditions and discuss potential consequences on texture perception and swallowing.

Symposium IR

Industrial Rheology

Organizer: Maryam Sepehr and Hossein Baghdadi

Monday 10:00 Room 207 IR1

The influence of particles on the rheology of monoclonal antibody solutions

Jai A. Pathak[1], Rumi R. Sologuren[1], and Rojaramani Anandakumar[2]
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Monoclonal antibody (mAb) formulations are increasingly developed as bio-therapeutics. Easing the dosing regimen for patients provides a key incentive to develop stable mAb solutions in the [mAb] range 100 mg/mL - 200 mg/mL. However, mAbs (proteins) have a propensity to aggregate in solution under such molecularly crowded conditions and become unstable. Protein solution viscosity data in the zero shear limit are

sensitive indicators of molecular stability in solution. Moreover, high shear rheology data are critical for self-injection device design. Therefore, I will discuss in this talk the influence of aggregate particles on the rheology system comprising mAb molecules dissolved at ~ 100 mg/mL in a surfactant-free buffer. Flow curve measurements at 5 and 23 deg C immediately after filtration through a 0.22 micron filter on to the cone-platen measurement geometry reveal that particles make a non-trivial hydrodynamic contribution: formulations containing particles have a viscosity that is one to two orders of magnitude larger than filtered solutions at low shear rates (between 0.01 and 0.1 1/s). At low shear stress O(0.1 Pa) filtered solutions display signatures of yield behavior in bulk flow curves. At asymptotically high shear rates O(1000 1/s) the viscosity of filtered and unfiltered formulations are practically equal, as particles and molecules offer minimal hydrodynamic resistance when oriented in the flow direction. The particles, characterized by bright-field optical microscopy, are predominantly filamentous (large aspect ratios), possibly due to dipole-dipole interactions amongst protein molecules in solution. Finally, I will examine the implications of low shear viscosity rise in particle-containing formulations for protein stability in solution.

Monday 10:25 Room 207 IR2

Effect of temperature on rheological properties of rubber materials in both the linear and the non-linear viscoelastic domains

Jean L. Leblanc

Polymer Rheology and Processing, UPMC - Paris-Sorbonne Universités, Vitry-sur-Seine 94408, France

It is well known that temperature effects are somewhat different in the linear and non-linear viscoelastic domains. Rubber materials are generally amorphous polymers so that in the room temperature range, they are on their rubbery plateau, largely above their glass transition temperature. Whilst they are generally processed above 100°C no phase change occurs during processing contrary to most thermoplastics. It follows that the (temperature) processing window of elastomers coincides with their usage window, and this is the main reason why these materials must be vulcanized to obtain useful objects. Rubber materials are generally so stiff that their rheological properties must be evaluated with special rheometers and closed-cavity dynamic torsional instruments have been proved over the last decades to be particularly suitable. With the adequate test protocols and data treatment, modern computer control rheometers allow the temperature dependency of rubber materials to be routinely assessed. The paper describes several test protocols developed for the Rubber Process Analyzer RPA 2000® to document the effect of temperature in both the linear and the nonlinear domains. Standard rheological properties, e.g. G*, G', G" and are considered in the linear domain, while relative harmonics as obtained from Fourier Transform are used in the nonlinear domains. For linear viscoelastic data, either the Arrhenius or the Williams, Landel and Ferry (WLF) models are used to treat temperature effects and both approaches are compared with respect to the (apparent) activation energy at a reference temperature. Results on various gum elastomers and several carbon black filled compounds are reported and discussed in details.

Monday 10:50 Room 207 IR3

RaPiD simulations of the rheology of pressure sensitive adhesives

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Most soft matter systems consist of particles which by themselves are too large to be simulated in full detail. In order to be able to simulate the rheological properties of such systems, only relevant time scales must be addressed and most degrees of freedom must be eliminated from the description. The elimination process introduces memory effects in the coarse description which renders simulations of realistic systems impossible. We will present a solution to this problem by keeping track of perturbations of the thermodynamic state of the eliminated variables. The resulting model, called RaPiD, is very generic and may be applied to study rheological properties of a large class of soft and composite matter. In this presentation we will report on RaPiD simulations of pressure sensitive adhesives. Such adhesives may be produced by emulsion polymerization obtaining latex particles of long acrylic polymers. On drying, the particles partly coalesce and form an adhesive film with rheological properties between those of viscoplastic solids and viscoelastic liquids. Despite the partial coalescence of the particles their rheological properties are dominated to a large extent by the chemistry of the interfacial regions. We will show that it is possible to quantitatively reproduce the shear and elongational properties of these systems by simulating a model in which each latex particle is represented by one deformable particle interacting both by thermodynamic and transient, non-equilibrium forces.

Monday 11:15 Room 207 IR4

Rheology and pH study of a model crystallizing surfactant system

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In previous work, we described the microstructure and rheology of model system formulations comprising (by weight) 9% sodium dodecyl sulfate, 3% cocamidopropyl betaine, and systematically varying amounts of palmitic acid in water at their natural pH (approximately 4-5). The systems were studied using the starch pasting cell rheometer tool, differential scanning calorimetry (DSC), and optical microscopy. This study revealed that sufficient palmitic acid was necessary (5-7%) for the model system to develop a macroscopic crystal network evidenced by solid-like rheological behavior. Both the storage modulus and yield stress showed a non-monotonic increase with an increase in the solids content; an unexpected drop in both parameters was observed as the solids level was increased from 10 to 12%. This transition was attributed to a change in crystal shape from long aspect ratio platelets to shorter aspect ratio platelets. To better understand the relationships among the microstructure, pH, and rheology of these fluids, sufficient amounts of potassium hydroxide were added to the model systems containing 5, 7, and 18% palmitic acid to adjust the pH to 6 and 7. The formulations with a pH of 6 behaved in a similar manner to the formulations without potassium hydroxide (at their natural pH). However, adjusting the model system pH to 7 resulted in no crystalline network formation and changes in the appearance of the crystals, which were more irregular in shape rather than plate-like. The ionization state of the molecules and the resultant change in crystal structure may provide some insight into the variation in macroscopic rheological behavior with pH. Both palmitic acid and cocamidopropyl betaine exhibit different ionization states depending on the pH. These different forms may lead to changes in molecular packing and, subsequently, affect the microstructure and macroscopic rheological behavior of the model system formulations.

Monday 11:40 Room 207 IR5

Slip and melt fracture of broad molecular weight metallocene high density polyethylenes

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The wall slip melt fracture behaviour of several broad molecular weight metallocene catalyst high density polyethylenes (HDPEs) are studied. It has been observed that for these resins the Cox-Merz fails. It is shown that this failure is due to wall slippage of the polymer melt on the die surface and could be captured using the Mooney technique. The calculated slip velocities show a power-law dependence on shear stress and scale with temperature and molecular weight. The melt fracture phenomena in the capillary extrusion of these polymers are also examined in detail. Some interesting correlations are found between critical shear stress for the onset of instabilities and molecular parameters of the resins which shed more light into the origin of these instabilities.

Monday Afternoon

Symposium BS

Rheology in Biological Systems

Organizers: Patrick Underhill and Alejandro G. Marangoni

Monday 1:30 Amphitheater A BS6

Analysis of red blood cells viscoelastic properties in microfluidic devices

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Red blood cells (RBCs) play the fundamental role of supplying oxygen to tissues by traveling through microcapillaries in microcirculation in vivo. The normal human red blood cells have a biconcave disk shape as long as they are not subjected to external stresses or constraints. However, when RBCs flow through capillaries with diameter comparable to cell size, they change their disk-like shape into a deformed one, resembling a bullet or a parachute [1]. The high RBC deformability is mainly due to the viscoelastic properties of the cell membrane, especially shear modulus and surface viscosity [2]. Alterations of RBC deformability are related to pathological situations and the resulting diseases are associated with microvasculature disorders. The experimental methods available include single cell techniques [3] and measurements on whole blood or diluted RBC suspensions in microcapillaries [4]. However, to our knowledge, microfluidic devices to determine the viscoelastic properties of RBC membrane are still lacking. In this work, a microfluidics system to investigate the flow behavior of red blood cells (RBCs) in a microcirculation-mimicking network of PDMS microchannels with thickness comparable to cell size is presented. By studying cell deformation in a divergent channel geometry, membrane viscoelastic properties are obtained from the application of the classical Kelvin-Voigt model. Possible applications include the analysis of RBC deformability in pathological situations, for which reliable quantitative methods are still lacking.

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Monday 1:55 Amphitheater A BS7

µPIV blood microflow velocity profile measurements: Comparison of the use of fluorescent particles versus RBC as tracer particles

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Micro-particle image velocimetry (µPIV) is a method of fluid flow measurement frequently used to investigate microcirculation and hemodynamics. For *in-vivo* studies (measuring the blood velocity profile in a microcirculation bed on living mammals) the current standard is to use red blood cells (RBC) as tracer particles for the µPIV method, while for *in-vitro* studies, micro fluorescent particles are sometimes added to the blood. The second method is theoretically much more precise due to the smaller size of the microparticles compared to the RBC. The goal of this project is to compare the two methods in a well-controlled *in-vitro* environment. Additionally, the effect of flow rate, channel size and blood hematocrit on the accuracy of the µPIV technique and the cross-correlation parameters are investigated. Tests are conducted in 20, 50 and 100 µm square microchannels to mimic the microcirculation but be fully repeatable. Porcine blood samples are prepared to obtain isolated RBCs which are then suspended in phosphate buffered saline (PBS) to specified hematacrit values. Higher hematocrits, including those approaching physiological values, prove difficult to work with due to the high density of RBC. This is in part due to the RBC tendency to form a cell-free layer at the edges of the channel, while the majority of the RBC move to the center. This density of RBC obscures the field of view, and cross-correlation proves difficult. The particles significantly decrease this problem. Adapting the correlation windows may alleviate this situation for the using the RBC as tracer particles. Velocity profiles in 2D are used to extrapolate 3D profiles in square channel and calculate flow-rate. We investigate the difference between the estimated shape of the velocity profile using fluorescent particles versus RBC as tracer particles.

Monday 2:20 Amphitheater A BS8

Flow induced segregation in suspensions of mixtures of deformable capsules in confined geometries using the boundary integral method

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Flow induced segregation in mixtures of deformable particles is relevant in many problems including in the separation or detection of diseased RBCs from their normal counterpart. These systems also serve as a model for investigating the flow behavior of drug delivery particles in circulation. In this work, we develop a fast O(NlogN) method for solving the Stokes flow boundary integral equation in an arbitrary geometry. The acceleration in the method is provided by the use of General Geometry Ewald Like Method (GGEM) for computing the Green's function in the geometry of interest. This algorithm is employed to study sheared suspensions of mixtures of deformable capsules with different rigidities in a slit geometry. Most results are presented for suspensions with a volume fraction of phi=0.2, with the constituent particles' capillary number being Ca=0.2 (stiff) and Ca=0.5 (floppy). It is found that in a suspension of primarily stiff particles, the mean wall normal position of both the stiffer and the floppy particle are comparable. With increasing concentrations of the floppy particle, the mean position of the stiffer particle shifts towards the wall. The particle concentration distribution along the channel height reveals that the stiffer particles tend to form a layered structure as evidenced by the presence of distinct peaks; the strength of the peaks closer to the wall increases with increasing concentration of the floppy particle. In contrast, the floppy particles exhibit a near singly peaked distribution around the centerline with weak signs of layering. A mechanistic theory is developed to explain the flow induced segregation in mixtures of deformable particles under confinement.

Monday 2:45 Amphitheater A BS9

Self-assembly of sickle cell hemoglobin: A dissipative particle dynamics simulation study

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The dynamics of self-assembled elongated step-like bundles of sickle cell hemoglobin has been investigated by dissipative particle dynamics (DPD) approach. Unlike implicit solvent models, the many-body energetic and hydrodynamic interactions are preserved naturally by incorporating explicit solvent particles in this approach. A coarse-grained model, which contains hydrophilic and hydrophobic particles, is constructed to match the structural properties and physical description (crowding affects assembly at high density) of sickle cell hemoglobin. The bending rigidity of the HbS fibers is controlled by harmonic spring and bond-bending interactions, and an additional bond-bending interaction among three successive hydrophobic and hydrophilic particles, combined with a torsional interaction between particles belonging to consecutive cross-sectional planes defined by two hydrophilic and two hydrophobic particles, is introduced to simulate the chain chirality of the proposed model. Our results show that chain chirality exerts a considerable influence on the self-assembly of sickle cell hemoglobin. In the absence of chain chirality, only small self-assembled micelles are observed in the DPD simulations because the coverage of hydrophilic particles on the surface of hydrophobic particles avoids intimate connections between hydrophobic and solvent particles. When we consider the chain chirality, local packing constraints due to chain chirality cause assembly to elongated step-like bundle micelles in order to minimize contact between the hydrophobic and solvent particles. These findings may be helpful in explaining how the sickle hemoglobin fibers are formed and in understanding the general principle of sickle cell hemoglobin.

Monday 3:35 Amphitheater A BS10

The microrheology of cancer cells and their metastatic potential

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The relationship among micromechanical properties of cancer cells, their environment and disease progression in cancer is quantified with microrheology and cell motility experiments with breast cancer cells. The mechanical stiffness of cancerous tissue is a key feature that distinguishes it from normal tissue and facilitates its detection clinically. While numerous inroads have been achieved toward elucidating molecular mechanisms that underlie cancer, quantitative characterization of associated cellular mechanical properties and biophysical attributes remains largely incomplete. This research provides insight into the following questions: (1) What is the effect of extracellular matrix (ECM) stiffness and architecture on internal cancer cell rheology and cytoskeletal organization? (2) What are the integrated effects of ECM stiffness and cell metastatic potential on the intracellular rheology and morphology of breast cancer cells? (3) What are the integrated effects of ECM stiffness, ECM architecture, and cell metastatic potential on the motility of breast cancer cells? Cancer-mimicking cells are cultured within synthetic ECMs of varying mechanical stiffness, where they are observed using time-lapsed confocal microscopy. Image analyses are employed to extract measures of cell migration speed and intracellular stiffness via particle-tracking microrheology. Major results show that ECM stiffness elicits an intracellular mechanical response only within the framework of physiologically relevant matrix environments and that a key cell-matrix attachment protein (the integrin) plays an essential role in this. Results indicate that the breast cancer-associated biomarker (ErbB2) is responsible for sensitizing mammary cells to ECM stiffness. Results also show that a switch in ECM architecture significantly hinders the migratory capacity of ErbB2-associated cells, which may explain why the ErbB2 biomarker is detected with much higher frequency in early stage breast cancer than in invasive later stage cancers.

Monday 4:00 Amphitheater A BS11

Matrix-induced alignment and shear flow: Effects on endothelial cells

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In straight segments of the blood vessel, the endothelium is aligned and the endothelial cells are resistant to inflammation and thrombosis. At bends and branches of the vessel where the endothelium is not aligned, however, the endothelial cells express adhesion molecules and chemokines that promote the adherence of platelets and leukocytes, leading to atherosclerosis. In this study, we aim to investigate the effects on the morphology and biology of endothelial cells due to the presence of an aligned matrix, with and without the presence of shear flow. Although it is known how shear flow can influence endothelial cells, the combination of matrix-controlled alignment and shear flow on endothelial biology (and morphology) is relatively unknown. While the phalloidin alignment and assembly of focal adhesions will help characterize the morphological effects on the cells, their biological function will also be evaluated. Proliferation, monocyte adhesion and integrin signaling are a few of the biological indicators of the endothelial cells that can indicate the effects of matrix-induced alignment and shear flow. Endothelial cells are cultured onto aligned and unaligned collagen substrates and then exposed to a continuous period of shear flow, perpendicular to the direction of collagen alignment. Afterwards, the morphology and biology of the endothelial cells are evaluated. Cells cultured on aligned collagen demonstrate a resistance to re-aligning themselves along the shear flow direction, while cells on unaligned collagen tend to elongate along the direction of shear flow. It is also expected that the endothelial cells on aligned collagen will express less adhesion molecules that prevent the adherence of monocytes. These observations may be especially significant in the development of vascular conduits, since endothelial cells are generally healthier if they can maintain their aligned orientation despite the turbulence of surrounding blood flow.

Monday 4:25 Amphitheater A BS12

Hydrodynamic behavior of tumor cells in a confined model microvessel

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An important step in cancer metastasis is the hydrodynamic transport of the so-called circulating tumor cells (CTCs) through blood microvessels. In vivo imaging studies in mice models show episodes of confined motion of tumor cells and trapping at microvessel bifurcations, suggesting that these hydrodynamic phenomena are important processes regulating CTC dissemination. Our goal is to use microfluidics to understand the interplay between tumor cell rheology, confinement and fluid forces that may help to identify physical factors determining CTC transport in microcirculation. We use leukemia cells as model CTCs and mimic the in vivo situation by investigating their motion in a confined microchannel. We also integrate a microfluidic manometer to measure time variations in the excess pressure drop during tumor cell motion. By analyzing the high-speed movies, variations in excess pressure drop, cell shape and cell velocity are simultaneously quantified. We find that the excess pressure drop is more sensitive to tumor cell velocity than shape index. In particular, the excess pressure drop increases with cell size and cell velocity. Interestingly, we find that the throughput of the technique is high enough (~ 100 cells/min) to assess tumor cell heterogeneity. Therefore, in addition to measuring the hydrodynamic response of tumor cells in confined channels, our results indicate that the microfluidic manometer device could be used for rapid mechanical phenotyping of tumor cells.

Monday 4:50 Amphitheater A BS13

Rheology of active-particle suspensions

Alexander Morozov and Davide Marenduzzo
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Suspensions of active particles have recently been demonstrated to exhibit a rich variety of non-trivial flow properties. Depending on the details of the hydrodynamics of particle's self-propulsion, their suspensions can be either shear-thinning or thickening [1]. It has even been suggested that at high enough activity, the viscosity of the system might vanish [2].

Here we combine analytics and hybrid lattice Boltzmann simulations to study linear and non-linear rheology of a model active liquid-crystalline fluid under steady and oscillatory shear. When the flow is assumed to be 1-dimensional we recover the previous results reported in [1,2]. However, in the regime of extreme shear-thinning we observe that hydrodynamic instabilities set in long before the viscosity is sufficiently reduced and the flow becomes 3-dimensional. Our observations suggest that the low-viscosity state of active suspension might be difficult to observe because their flows easily become unstable.

1. Y. Hatwalne et al., Phys. Rev. Lett. 92, 118101 (2004); 2. L. Giomi et al., Phys. Rev. E 81, 051908 (2010).

Monday 5:15 Amphitheater A BS14

Rheology of active fluids

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Active fluids have become a highly topical research area at the interface of complex fluids and biological physics. Such systems differ from their passive counterparts in that particles absorb energy and generate motion. Examples include bacterial suspensions, in vitro mixtures of cytoskeletal filaments and motor proteins, and vibrated granular rods. In this talk, I will present a kinetic model for active fluids and analyze the behavior of such a system subjected to a weak steady and oscillatory shear. We explore the steady states, perform their stability analysis and predict the rheology of active fluids including an activity thickening or thinning behavior of the apparent viscosity and a negative apparent viscosity depending on the particle type, flow alignment and the anchoring conditions. We find dualities which show that flow-aligning rodlike contractile (extensile) particles are dynamically and rheologically equivalent to flow-aligning discoid extensile (contractile) particles for both tangential and homeotropic anchoring conditions. We investigate the role of the concentration of active fluids in controlling the rheological behavior: the apparent viscosity may decrease with the increase of the concentration. When the steady shear is replaced by an oscillatory shear, phase locked modes and linear viscoelasticity as well as an inverse problem are also discussed.

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Monday 1:30 Amphitheater B SC6

The relation between shear flow and extensional flow of non-Brownian shear-thickening fluids

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We contrast the extensional and shear dynamics of non-Brownian suspensions as a function of particle concentration. We show that the thinning rate selected during the viscoelastic pinch-off of a liquid bridge is related to the shear rate at which normal stresses become positive, which differs from the shear rate at the onset of shear thickening. By tracking particles, we demonstrate that the extensional flow is heterogeneous, with local variations of the volume fraction consistent with self-dilution. This non-uniform structure is the cause of the buckling of the threads formed after break-up.

Monday 1:55 Amphitheater B SC7

Shear thickening and jamming in dense suspensions of different particle shapes

Eric M. Brown[1], Hanjun Zhang[2], Nicole A. Forman[2], Benjamin W. Maynor[3], Douglas E. Betts[3], Joseph M. DeSimone[2], and Heinrich M. Jaeger[1]

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We measured viscosity curves of densely packed suspensions with a variety of particle shapes, including rods of different aspect ratios and non-convex hooked rods which were fabricated by the PRINT process. Each suspension exhibits similar Discontinuous Shear Thickening in which the slope of the stress-shear rate relation increases with packing fraction &phi and becomes discontinuous in the limit of the jamming transition at &phi$_c$, above which the suspensions behave as yield stress fluids. Normal stresses and shear stresses are found to be strongly coupled by a frictional relation, suggesting the shear thickening is a result of dilatancy. While the value of &phi$_c$ varies with particle shape, the slopes of the stress-shear rate relation collapse onto the same curve as a function of &phi/&phi$_c$ for each convex shape, suggesting the jamming transition controls the shear thickening like a critical point. Intriguingly, the slopes for non-convex hooked rods do not collapse onto the same curve as for convex particles, instead showing strong shear thickening over a wider range of packing fraction.

Monday 2:20 Amphitheater B SC8

Shear thickening of chemical mechanical polishing slurries using high shear rheology

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Chemical mechanical polishing (CMP) is a fundamental technology used in the semiconductor manufacturing industry to polish and planarize a wide range of materials for the fabrication of microelectronic devices (i.e., computer chips). The CMP slurry is a mixture of colloidal abrasive, carrier liquid (usually water) and active chemicals that react with the material to be removed. During the polishing process, the slurry will undergo shear rates in excess of 10^6 s^{-1}. Under this extreme shear environment, it is hypothesized that individual slurry particles collide with one another forming large agglomerates (>0.5 μm) that cause the slurry to display dilatant behavior. These agglomerates trigger the formation of defects such as scratches, gouges, pits, and corrosion during polishing. On the order of 10-15% of failed integrated circuits can be linked to CMP induced defects which is estimated to cost the semiconductor industry $4.5 to $9 billion annually in lost production.

The slurries of interest are a concentrated fumed silica suspension in water with added KOH. Utilizing high shear rheology to mimic the CMP process, our objective is to obtain a detailed understanding of the changes to particle structure, both temporary and permanent, associated with the shear thickening response of CMP slurries. A controlled stress rheometer with a parallel plate geometry at small gaps measures the non-linear rheological responses of the high solids slurry. Rheo-SALS was used to identify the formation, shape, and size of micron sized structures generated under shear. The shear thickening behavior of the CMP slurries was altered with the addition of aqueous electrolytes (LiCl, NaCL, KCl, and CsCl) and a decrease in critical shear rate and shear stress was witnessed with increasing electrolyte concentration.

Monday 2:45 Amphitheater B SC9

Imaging the microscopic structure of shear thinning and thickening colloidal suspensions

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The viscosity of colloidal suspensions can vary by orders of magnitude depending on how quickly they are sheared. Although this non-Newtonian behavior is believed to arise from the arrangement of suspended particles and their mutual interactions, microscopic particle dynamics in such suspensions are difficult to measure directly. Here, by combining fast confocal microscopy with simultaneous force measurements, we systematically investigate a suspension's structure as it transitions through regimes of different flow signatures. Our measurements of the microscopic single-particle dynamics unambiguously show that shear thinning results from the decreased relative contribution of entropic forces and that shear thickening arises from particle clustering induced by inter-particle hydrodynamic lubrication forces. This combination of techniques illustrates an approach that complements current methods for determining the microscopic origins of non-Newtonian flow behavior in complex fluids.

Monday 3:35 Amphitheater B SC10

Rheo-physics of shear thickening fluids (STF) studied with large amplitude oscillatory shear (LAOS)

A. Kate Gurnon and Norman J. Wagner
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Shear Thickening Fluids (STFs) are concentrated colloidal suspensions that exhibit increases in viscosity under high shear rates of deformation. Previous work investigating colloidal suspensions using oscillatory deformation to probe the viscoelastic state of the material has focused on the analysis of the first harmonic response (G' and G") and the associated shear and/or frequency thickening. Additional information about the material's response during LAOS is contained in higher harmonic stress contributions, which are neglected in the simple analysis. This work focuses on LAOS results of a model STF suspension [Kalman, D.P. and N.J. Wagner, Rheol. Acta. 2009, 48:897-908] analyzed using two methods developed for physical interpretation of the mechanical response of the suspension [Ewoldt, R.H. et al. J. Rheol. 2008, 52, (6), 1427-1458 and Wilhelm, M. et al. Rheol. Acta. 1998, 37:399-405]. The two methods for LAOS interpretation are compared and analyzed. An understanding of the microstructural rearrangements of STF during steady shear deformation developed via rheo-SANS is extended and applied to STFs during the alternance state of LAOS. We find the results suggest maximal hydrocluster formation in the middle of the deformation cycle. A basic microstructural understanding of an STF's oscillatory stress response is achieved and used in the development of model constitutive equations for STFs.

Monday 4:00 Amphitheater B SC11

A comparative LAOS study of yielding and flow in soft glasses

Nick Virgilio[1], Dimitris Vlassopoulos[2], and Michel Cloitre[3]
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Soft glasses encompass concentrated dispersions, typically made of soft and deformable particles packed into an amorphous glass-like structure. These materials exhibit generic rheological properties intermediate between solid and liquid. They behave like slowly evolving elastic solids at rest, but beyond a critical stress value they yield and flow with a complex dependence on shear rate. While it is often considered that these properties are universal, it remains unclear whether and how the great variability of compositions and architectures in these materials plays a role.

Here, we take advantage of a newly developed LAOS methodology [1] to compare the yielding and flow properties of different systems that encompass, in our view, many features of soft colloids: crosslinked microgels, self-assembled block copolymer micelles and multiarm star polymers. We interpret the stress waveforms as temporal juxtapositions of physical processes, allowing us to probe cage elasticity, dynamic yielding, flow, as well as aging and rejuvenation from individual cycles of deformation. The results show that each system has a specific signature, which highlights the importance of the local architecture with respect to the macroscopic rheology and in particular the solid-liquid transition.

[1] S. Rogers, B. Erwin, D. Vlassopoulos, M. Cloitre, J. Rheol. 55, 435 (2011)

Monday 4:25 Amphitheater B SC12

LAOF: large amplitude oscillatory flow, a microstructural perspective

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The literature is teeming with experimental studies of the response of materials, from the common (colloidal dispersions and polymer melts) to the exotic (slug mucus), to large amplitude oscillatory shear flows (LAOS) as well as the behavior of various constitutive models when forced in the same fashion. We have conducted a detailed study of the response to large amplitude oscillatory flows from a micromechanical perspective (the dilute microrheology of colloidal dispersions). The suspension microstructure, satisfying the Smoluchowski equation, is decomposed into temporal normal modes which are coupled together by the imposed flow. The solution for these coupled structure functions provides considerable insight into the physical processes involved in large amplitude flows, in particular, the competition between hydrodynamic and thermal forces. In the linear response regime, hydrodynamic forces are always in phase with the imposed flow so that thermal forces govern variation in the material response across the frequency spectrum. The same is not true in the non-linear regime where thermal relaxation processes are slow relative to the imposed flow, and hydrodynamic flows provide the dominant dissipative mechanism. We observe directly the effects of phase lag in the hydrodynamic forces due to the interplay of temporal distortions in the suspension structure and hydrodynamic interactions. Surprisingly, this is a form of hydrodynamic loading wherein the hydrodynamic interactions among the particles act over short periods of time to enhance the rate at which the suspension would relax back to equilibrium.

Monday 4:50 Amphitheater B SC13

Applications of Rheo-PIV to oscillatory shear of model crude oils

Christopher J. Dimitriou[1], Rama Venkatesan[2], and Gareth H. McKinley[1]
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In this talk, the rheological behavior of several model crude oils is experimentally studied at temperatures below their wax appearance temperature (WAT). We first consider a two-component wax-oil system that has been examined in previous studies under steady shearing conditions using a combined approach of bulk rheometry and localized velocimetric measurements (RheoPIV). An extension of this work is presented in which the progressive yielding of this class of wax-oil systems is studied under oscillatory flow. In particular, Large Amplitude Oscillatory Shear (LAOS) is used in order to map out the non-linear behavior of the material. Along with this, simultaneous local velocity measurements within the fluid are carried out using Particle Image Velocimetry (PIV). The capabilities of the Rheo-PIV apparatus allow deviations from a linear velocity profile to be determined within a single cycle of oscillatory shear and continuously monitored over several cycles. These deviations can also be correlated to simultaneous measurements of the oscillating stress-strain response of the fluid. The combination of LAOS and local PIV measurements also allows for a more in-depth study of the yielding mechanisms and stress-dependent wall-slip in the model wax-oil system. The second part of this work deals with the development of a model water-oil-wax system for use in rheometric studies of water/crude oil emulsions. In this three-phase system the wax crystallites can help stabilize the mixture and the emulsified water droplets substantially modify the viscoelastoplastic nature of the material. Large amplitude oscillatory shear flow provides a mechanism for monitoring these changes. These multicomponent systems also present new challenges for the application of RheoPIV techniques - their semi-opaque nature renders traditional particle tracking techniques based on light scattering ineffective and requires new imaging strategies.

Monday 5:15 Amphitheater B SC14

Surface driven-organization in liquid crystal nanodrops

Juan P. Hernandez-Ortiz[1], Vivek Tomar[2], Saul I. Hernandez[2], Jose A. Moreno-Razo[3], and Juan J. de Pablo[2]
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The structure of nematic liquid crystals confined in a spherical nano-droplet is examined using a combination of many-body molecular dynamics simulations and a continuum molecular theory. Surface anchoring conditions, homeotropic or planar, are modified according to the local surfactant-to-water ratio at the droplet's surfaces. Phases and structure are studied as a function of temperature and total surfactant coverage. For the continuum theory an Euler-Lagrange approach is used, where the free energy functional of an order tensor parameter is minimized using a Ginzburg-Landau relaxation. In addition, a diffusion equation is solved at the surface for the surfactant-water ratio. A unsymmetric radial function approach is used for the numerical approximation. The molecular dynamics simulations rely on Gay-Berne type potentials to model liquid crystal and surfactant molecules. The confinement of nematic liquid crystals within nano-droplets creates remarkable bulk-to-surface self-organization, contrary to the regular surface-to-bulk self-organization. The nematic drives the formation of patterns and non-homogeneous regions at the droplet surface. This patterns appear as a response of the minimization of the liquid crystal free energy functional, which drives diffusion in a Nernst-Planck-like fashion. Theoretical predictions and molecular simulations are in quantitative agreement,thereby lending credibility to the predictions presented in this work.

Symposium SI

Surface and Interfacial Rheology

Organizers: Jan Vermant and Eric Weeks

Monday 1:30 Founders Ballroom A SI6

Transport and interfacial rheology of polymer-grafted nanoparticles at air-water and oil-water interfaces

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Particle stabilized emulsions, or Pickering emulsions, offer a number of advantages over traditional surfactant stabilized emulsions. Since the binding energy of a particle at an interface is proportional to the square of the particle radius, nanoparticles are less effective stabilizers than micron sized particles due to lower binding energies. However, polymer grafted nanoparticles are particularly effective emulsifiers; stabilizing at very low added concentrations of particles. Grafted nanoparticles do lower the interfacial tension when adsorbed, which is not a feature of most Pickering emulsions. In this work, we characterize the interfacial transport of polymer-grafted nanoparticles to the air-water and oil (xylene)-water interface and attempt to understand the key mechanism of stabilization. We measure static and dynamic interfacial tension at the air-water and xylene-water interface and quantify the rates of diffusion of polymer grafted nanoparticles to the interface. Driven by the observation that, in surfactant-stabilized emulsions, a correlation exists between dilatational elasticity of the interface and emulsion stability we quantify the interfacial elasticity of grafted-nanoparticle laden interfaces using forced sinusoidal oscillations of the interface. We present a systematic study of two grafted nanoparticle systems that form stable emulsions at the xylene-water interface. The results are put into the current framework of analogous surfactant and particle studies of dilatational elasticity and interfacial rheology.

Monday 1:55 Founders Ballroom A SI7

Porous media model and collective behaviour of colloidal particles trapped at a fluidic interface

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It is well known that charged colloidal particles may form an effective two-dimensional suspension at a fluidic interface. To understand the dynamics and collective behaviour of this system is at the core of a better understanding of the Pickering emulsion, which has a broad range of practical applications. Many experiments have been completed where two interfaces were brought into contact in a controlled manner and various observations, including particle zipping and bridging, have been made to understand the stabilisation mechanism of the Pickering emulsion. In this work, we propose to explain the observations in the literature with a combined experimental and theoretical approach. Given the interactions between the colloidal particles , we first simulated the motion of the colloidal particles at the water-decane interface with Brownian Dynamics simulation, assuming pair-wise interactions using all known physical constants of the system. In this context, we have also incorporated a porous media model that relates the particle velocity to the local surface coverage through the effective permeability of a porous media. At the same time, we performed real-time experiments where two particle-laden water-decane interfaces were brought into contact, following the procedures detailed in the literature. The BD simulation results are then compared to the real-time microscopic images recorded on the CCD camera and analysed using MATLAB. With the appropriate porous media model, the simulation is able to capture the aggregation-evacuation phenomena prior to the particle bridging and eventual coalescence.

Monday 2:20 Founders Ballroom A SI8

Graphene oxide sheets at planar interfaces: Interfacial rheology and structural characterization

Luna Imperiali d'Afflitto[1], Christian Clasen[1], Jan Fransaer[2], Christopher W. Macosko[3], and Jan Vermant[1]
[1]Department of Chemical Engineering, Katholieke Universiteit Leuven, Leuven, Belgium; [2]Department of Materials Science, Katholieke Universiteit Leuven, Leuven, Belgium; [3]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, United States

Graphene oxide sheets have been shown to be a viable precursor for graphene in high-tech applications, because of both its cost-effective production and its hydrophilic nature, which allows dispersing the particles in an aqueous environment. Nevertheless, in order to produce graphene-based materials, one critical step is the directed self-assembly of single sheets into controlled structures. In this regard, templating the structure by fluid interfaces represents an ideal assembling tool for sheets, since the bi-dimensional nature of these particles can be exploited. In the present work we investigate the behavior of graphene oxide sheets at fluid interfaces: we show that graphene oxide is a strong surface-active material and that sheets assemble at the interface to form exceptionally stable and compact monolayers. The elastic properties of such interfacial assemblies are investigated with interfacial shear rheology in combination with an analysis of the buckling instability that develops in the compressed monolayers. Furthermore, the assemblies are deposited from the interface using a Langmuir-Blodgett technique and the structure is characterized by means of different microscopy techniques (optical microscopy, AFM, Fluorescence Quenching Microscopy). We argue that the exceptional mechanical properties measured for interfacial assemblies arise from the unexpected peculiarity of graphene oxide sheets to avoid

overlapping even at high interfacial compressions. This property could yield an alternate strategy for producing films of graphene oxide and graphene.

Monday 2:45 Founders Ballroom A SI9

Bulk and interfacial rheology of the tear film

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Meibomian lipids are of great interest due to their association with a stable tear film. They are a mixture of nonpolar species such as long-chain wax esters, cholesterol esters and fatty acids and are traditionally thought to form ~100nm thick blanket over the aqueous part of the tear film. As the outermost layer of the tear film, it is believed that the lipid layer is responsible for promoting tear film mechanical and structural stability. The challenge with taking bulk rheology measurements of human meibum is the very small sample size (on the order of 2 microliters). The bulk properties such as viscosity and moduli were being conducted using a stress rheometer with small tooling that was adjusted such that it can accommodate sample volume of 1-2 microliters. They interestingly reveal that the elastic modulus, exceeds the viscous modulus, for temperatures even above the melting transition. In addition, the melting transition is very dramatic and has the moduli increasing by more than three orders of magnitude as the sample is cooled. Small angle x-ray measurements reveal a co-crystalline structure where only one crystalline component melts as physiological temperatures are approached and this supports the bulk rheology measurements. The interfacial rheology measurements of thin meibomian lipid layers at the air-water interface was accomplished with interfacial stress rheometer (ISR) and it was discovered that these films are remarkably viscoelastic. Along with these findings we studied the influence of surface viscoelasticity on the dynamics of the moving contact line as drops covered with thin films of meibomian lipids translate across a surface. It was found that while monolayer coating of a non-elastic surfactant did not change the behavior of the moving contact line from its classical response, the interfacial viscoelasticity of the meibomian lipids induced a strong "stick-slip" motion.

Monday 3:35 Founders Ballroom A SI10

Interfacial shear rheological behaviors of natural silk fibroin

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The interfacial viscoelastic behavior of natural silk fibroin at air/water and different oil/water interfaces was investigated by interfacial shear deformation. The coexistence of distinct hydrophobic and hydrophilic regions endows natural silk fibroin molecules with amphiphilic character and surface activity, making this molecule able to form stable viscoelastic films at the interface of an aqueous medium with either air or oil. This character suggests silk fibroin could have important potential applications in drug delivery systems and cosmetics as an effective emulsion stabilizer due to its excellent mechanical properties and biocompatibility. At both air/water and oil/water interfaces, the silk fibroin can form stable, solid-like interfacial gels with ordered beta-sheet structures after protein conformation rearrangement and intermolecular self-assembly at the interface. The resulting interfacial moduli are remarkably large and increase with silk fibroin concentration. Due to the increased compatibility between the hydrophobic domains of silk fibroin and oil molecules, the silk fibroin interfacial gel generated at the oil/water interface is more stable, stronger and tougher than that at the air/water interface, possessing greater interfacial yield strain and higher recovery ability after the nonlinear fracture. Films deposited by Langmuir-Blodgett deposition were studied by scanning electron microscopy (SEM) and x-ray diffraction to reveal a fibrous structure at the interface. It is verified that silk fibroin can stabilize the O/W emulsions with oils of different polarity, and increasing fibroin concentration and oil polarity are helpful for getting more stable emulsion. The average droplet size decreases with the increase of fiber concentration or oil polarity and the decrease of oil volume fraction.

Monday 4:00 Founders Ballroom A SI11

Morphological and mechanical properties of recombinant protein interfaces

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Proteins diluted in an aqueous solution, adsorb spontaneously to any interface be it air, liquid, or solid and thereby form a stable viscoelastic adsorption layer [1, 2]. This process can be applied for the encapsulation of active agents into containers with a soft protein shell. In this study we correlate the structure, stability and surface activity of a set recombinant proteins to the resulting properties of the adsorption layer at the air/liquid interface. A further question that is assessed is whether the proteins remain native or unfold at the interface and to which extend this process affects the adsorption layer morphology and viscoelasticity. For this purpose we applied two recombinant proteins from the Designed Ankyrin Repeat protein (DARPin) family [3,4]. The two molecules are composed of two terminal-cap building blocks and a different amount of internal-repeat building blocks. We have shown that by changing the size and stability of the protein the adsorption layer stability can be adjusted. The more prone the protein to unfolding the more stable the adsorption layer formed by this protein [5]. Small angle X-ray and neutron scattering experiments at the air/liquid interface were performed to gain structural information on the protein adsorption layer. The findings of the above experiments could allow the prediction of the adsorption behavior of the entire DARPin family members of which are used for pharmacological purposes [6]. Furthermore, the variable degree of protein stability can be exploited for the adjustment of the viscoelasticity of capsules composed of tailored proteins.

[1] Murray BS: Curr. Opin. Colloid Interface Sci. 16 (2011) 27-35. [2] Erni P *et al.*: Macromol. Mater. Eng. 296 (2011) 249-262. [3] Binz KH *et al.*: J Molec Biol 332 (2003) 489-503. [4] Wetzel SK *et al.*: J Molec Biol 376 (2008) 241-257. [5] Mitropoulos V *et al.*: Soft Matter, 10.1039/c1sm05256j. [6] Stumpp MT *et al.*: Drug Discov Today, 13 (2008) 695-701.

Monday 4:25 Founders Ballroom A SI12

Anomalous coalescence in sheared 2D foam

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We report an experimental study on shearing a monolayer of monodisperse bubbles floating on liquid in a narrow gap Couette device. The bubbles in such a "bubble raft" coalesce only if the shear rate exceeds a threshold value. This is in contrast to the conventional wisdom that bubbles and drops coalesce for gentler collisions, at shear rates below a critical value. Furthermore, we have found that the threshold shear rate increases with the bubble size and the viscosity of the suspending liquid, but not with the bulk surfactant concentration as long as it is above the critical micelle concentration. Through visualization and scaling arguments, we have advanced an explanation of the anomalous behavior in terms of centripetal forces on the bubbles, which compress the bubbles radially inward and accelerate film drainage. The scaling relationship thus derived correlates well with experimental data.

Monday 4:50 Founders Ballroom A SI13

Rheology of ultrathin polymer films: Biaxial inflation vs. liquid dewetting

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The viscoelastic response of ultrathin polymer films remains an area of great interest because these systems can show greatly reduced glass transitions, often attributed to a highly mobile surface layer. Direct viscoelastic measurements of the thin films offer the possibility of directly observing these surface rheological effects. Here we present results from measurements of the viscoelasticity of films of polycarbonate and polystyrene with thicknesses as low as 3 nm in the former case using two different methods. First, we present the viscoelastic results from membrane inflation measurements using the TTU bubble inflation method in which films are suspended over micron dimension channels in filter membranes and inflated. The growth of the bubbles is monitored with an atomic force microscope and analyzed using classical methods. The second method is the liquid dewetting method pioneered by Bodiguel and Fretigny[1]. Here we place the ultrathin films of polystyrene and polycarbonate onto a hot glycerol surface and, because of a favorable spreading parameter, the films dewet. The film geometry is monitored optically as a function of time and the creep response of the materials can be obtained as the surface tension drives the dewetting as a biaxial compression test. The results of the bubble inflation method and those of the liquid film dewetting method are different and those differences will be discussed. In addition, the behaviors of polystyrene and polycarbonate are different, with the polycarbonate showing greater reductions of glass transition than the polystyrene in the bubble inflation experiment and a more modest reduction in the thin film dewetting experiment where the polystyrene does not show a significant reduction in the glass transition. The significance of these results will be discussed.

1. H. Bodiguel and C. Fretigny, "Reduced viscosity in thin polymer films," Physical Review Letters, 97, 266105 (2006).

Monday 5:15 Founders Ballroom A SI14

The development of an innovative triborheometry fixture/design to study the frictional dynamics of solid-liquid systems

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This paper describes an innovative triborheometry fixture/design to study the frictional dynamics of several solid-liquid systems, such as skin substitute/lubricants, PDMS elastomer/silicon oil and other natural products, for example banana skin peel. The triborheometry fixture/design includes various hardware components; probably the most important are the helical springs of different stiffnesses. The fixtures are adapted to a commercial rheometer and the experimental set-up would be modified according to the system to test. By altering process conditions the effect of surface roughness/lubricant fluid would enable us to measure the coefficient of friction at different angular velocities and contact stresses for the different solid-liquid systems. In this paper, experimental details for the triborheology tests along with materials response are presented. From the data, quantitative explanations for the Beam/Disc-coupling and material-structures design are given.

Symposium MB

Rheology of Polymer Melts and Blends

Organizers: Joao Maia and Avraam I. Isayev

Monday 1:30 Founders Ballroom B MB6

Nanoparticles in polymer melts: Size and dispersion effects

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Nanoparticle (NP) size and dispersion state critically affect the properties of polymer nanocomposites (PNCs). Here we consider two systems. In the first system we have polystyrene (PS) grafted silica NPs, 14nm in diameter in a PS matrix. These particles behave as amphiphiles, and the grafted chain length, matrix chain length, and grafting density determine their degree of miscibility with the PS matrix. Alternatively we consider a system of silica NPs in poly(2-vinyl pyridine) (P2VP). Here the NP and P2VP have a strong interaction, but the dispersion can still be controlled by proper solvent casting of the material; we use varying amounts of pyridine to charge stabilize the particles in solution and thus vary the dispersion state. We further use this second system to study NP size effects on PNC properties. In each case we attempt to isolate the rheological effects of the NP network from those of the PS or P2VP matrix. We use SAXS and TEM to probe PNP structure and NP dispersion state, and thermogravimetric analysis is also used to quantify the bound polymer layer available for participation in a polymer-particle network.

Monday 1:55 Founders Ballroom B MB7

Nanoparticles in polymer melts: Dynamics of polymers and the nanoparticle network

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Silica nanoparticles (NPs) are dispersed in solution by adding pyridine that accepts a proton from the silica surface, imparting charge-stabilization. Poly(2-Vinyl Pyridine) is then added and this polymer displaces the pyridine, leaving P2VP strongly bound to the NP surface. The solvent is removed to make a P2VP/silica nanocomposite that is truly stable in the sense that the bound layer of P2VP prevents direct contact between NPs. Reasonably monodisperse silica NPs are used, with sizes ranging from 14 nm to 100 nm. Segmental dynamics of P2VP are studied using dielectric relaxation spectroscopy and the terminal dynamics of P2VP and the nanoparticle network are probed using linear viscoelastic methods. For nanocomposites with large amounts of surface area per unit volume (i.e., 14 nm NPs at high loadings) the segmental relaxation dispersion is broadened significantly, suggesting that the bound layer of P2VP is slower than the bulk P2VP. Such nanocomposites also have a clear nanoparticle network that controls their terminal dynamics in oscillatory shear and stress relaxation experiments. The roles of segmental dynamics and entanglement between adsorbed chains on the viscoelastic response of the nanoparticle network will be discussed.

Monday 2:20 Founders Ballroom B MB8

The effect of flow and confinement on the placement of non-spherical nanofillers in polymer melts: Simulation and experiment

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Non-spherical nanofillers such as nanorod, nanorwire, and carbon nanotube (CNT) are often incorporated into a polymer matrix to enhance its functionality. Alignment and dispersion of these nanoparticles are crucial in achieving desired material properties such as thermal and electrical conductivity, and mechanical properties. First, we used coarse-grained molecular dynamics (MD) simulation to quantitatively examine the effect of shear, elongation, and confinement on the alignment and dispersion of model nonspherical nanoparticles in polymer matrices. Our simulation results reveal that the enhanced dispersion of nanorods by shear flow drastically diminishes as the aspect ratio of nanorod increases. However, the incorporation of attractive spherical nanoparticles into the nanorod/polymer system can improve the dispersion of nanorods and their alignment along the flow direction. Under elongation, we observed much better dispersion and alignment of nanorods along the flow direction than under shear flow. When selective nanorods were placed in cylindrically confined block copolymer (BCP) melts, the nanorods were aligned parallel or perpendicular to cylinder axis depending on the degree of cylindrical confinement. We also performed equivalent experiments to confirm the validity of our simulation studies. For elongation experiment, polycarbonate (PC) solution with various aspect ratios of CNT after sonication was electrospun to yield PC/CNT nanofibers with well-dispersed and well aligned CNTs. Finally, gold nanowires were incorporated in Polyisoprene-b-Polystyrene (PI-b-PS) BCP and electrospun to study the placement of non-spherical nanofillers in cylindrically confined BCP. These experimental results are in good agreement with predicted simulations, suggesting that coarse-grained MD simulation can be used as a predictive tool for controlling the placement of non-spherical nanofillers in a polymer matrix under flow and confinement.

Monday 2:45 Founders Ballroom B MB9

The viscoelastic properties of layered silicate filled corn protein (zein) nanocomposite moldable resins

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Zein, a prolamine found in corn is a biodegradable material able to form films with potential applications in coating and packaging industries. To enhance the physical properties of zein films, polymer layered silicate nanocomposite technology has been used. The hybrid of zein and layered silicates were prepared into intermediate moldable resins that later are blown into thin films by extrusion with a blowing head. The aim of this study was to investigate the viscoelastic properties of the zein layered with increasing levels of silicate nanomaterials. The hybrid resins were characterized by dynamic oscillatory shear measurements. Frequency sweeps were obtained in the linear viscoelastic range of the material as a function of layered silicate content (0%-9%). Both storage and loss moduli increased as layered silicate content increased in the zein matrix. The creep compliance of hybrid resins decreased with increasing layered silicate concentration. Moreover, the nonlinear viscoelastic properties of the hybrid resins were also investigated. The Wagner constitutive model was used to predict the steady shear properties from the experimental linear stress relaxation and a damping function obtained from the strain dependence of moduli in the non-linear region. There was excellent correspondence between the experimental data and the predictions of the Wagner model.

Monday 3:35 Founders Ballroom B MB10

A new generation dual controlled-stress/rate extensional rheometer for polymer melts

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Over the last 30 years, extensional rheometry has been continually at the forefront of research in rheometry because of its relevance to real-world flow situations and the difficulty in performing well-controlled, physically relevant experiments. Our group has been working in this area, having developed its own experimental capability in the form of a controlled-rate extensional rheometer that is based on the Meissner principle of extension between pairs of counter-rotating rollers while keeping sample length constant, albeit in our case the extension is only performed at one end, and adapts onto a commercial rotational Weissenberg rheogoniometer. Recently we introduced a second generation instrument working under the same basic principle but able to perform experiments in true controlled stress mode via a feedback control loop that monitor the cross section of the sample in time and adjusts the applied torque in order to keep the stress in the material constant.We introduce our third generation, the CSER - Controlled Stress Extensional Rheometer, which is a dual controlled-stress/rate extensional rheometer for high viscosity systems, with two pairs of counter-rotating rollers to ensure deformation homogeneity and can fit into the oven of conventional rotational rheometers. Due to its unique combination of geometrical set-up and feed-back control loop it now is possible for the first time to perform experiments on polymer melts both in controlled rate and controlled stress modes up until the point of physical rupture, whilst guaranteeing optimal deformation homogeneity, which is not the case with other instruments such as the SER, the Munstedt type of rheometers and even our previous ones.

Monday 4:00 Founders Ballroom B MB11

Flow and failure of monodisperse and bidisperse polymer melts in controlled stress uniaxial extensional flow

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In this work we use our new CSER, a dual controlled-stress/rate extensional rheometer, to study the flow and failure behavior of model monodisperse and bidisperse styrene-butadiene random-copolymer (SBR) melts, recently studied in the literature in controlled strain mode [1]. This rheometer was developed for polymer melt testing, is not limited in maximum Hencky strain, like the SER and filament stretching rheometers are, and thus can test small material samples up to failure and/or rupture [2]. In particular, we will study the elongational behavior of these systems up until the point of physical rupture, under optimal deformation homogeneity, in both stress and strain controlled situations, which is possible due to the CSER's unique combination of geometrical set-up and feed-back control loop. This work will be compared with results from the SER, and will allow a unique insight to be gained on the dynamics of chain disentanglement and/or disintegration.

References: [1] Wang Y., S. Cheng, and S. Q. Wang, "Basic characteristics of uniaxial extension rheology: Comparing monodisperse and bidisperse polymer melt", submitted to J. Rheol, 2011. [2] Andrade, R.J. and J. M. Maia, "A study on the flow, failure and rupture mechanisms of branched polyethylene in controlled-stress uniaxial extensional flow", J. Rheol. 2011, in press.

Monday 4:25 Founders Ballroom B MB12

Non-Gaussian stretching behavior of entangled polymers

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The behavior of entangled SBR melts and solutions in rapid uniaxial extension has been studied by rheometric and rheo-optical measurements. A yield-to-rupture transition occurs around the same Rouse Weissenberg number of nine for all samples when the failure mechanism changes from chain disentanglement (yielding) to chain scission. Our results show that rupture takes place only when chains between entanglements are near full extension, the strain at rupture grows with increasing entanglement spacing, and the critical stress for rupture is proportional to the polymer concentration. These characteristics are consistent with the representation of entangled polymers in terms of a transient network.

Monday 4:50 Founders Ballroom B MB13

In situ x-ray scattering studies of ordered block copolymer melts during uniaxial extensional flow

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In situ x-ray scattering methods have been broadly applied to study the structural dynamics of polymers and other complex fluids under flow, and can provide deep insights into the microstructural origins of complex non-Newtonian flow characteristics. Most studies in this vein have employed either homogenous shear flow, or processing flows such as fiber spinning which are complicated by inhomogenous deformation histories and/or nonisothermal operation. Here we present the design and implementation of a new apparatus for in situ x-ray scattering studies of polymer melts during homogenous uniaxial extensional flow. The experiment is based on the commercially-available SER extensional flow fixture, which employs two counter- rotating drums to deform a sample strip of polymer melt. This fixture has been incorporated into a custom-fabricated convection oven designed to facilitate x-ray access to the sample, and operation in a typical synchrotron beam line environment. To illustrate the capabilities of this device, we report measurements of flow-induced structural changes in cylindrically ordered styrene-ethylene butylene-styrene triblock copolymers. At early stages, small-angle x-ray scattering data reveal that the ordered microstructure deforms affinely until Hencky strains of ~ 0.2 are reached. A global re-orientation process leads to orientation of microdomains predominantly along the stretching direction after Hencky strains of ~ 1. Subsequent stretching does not lead to further qualitative changes in two-dimensional SAXS patterns. Relaxation of microdomain orientation is observed following cessation of extensional flow. The in situ SAXS data are compared with off-line measurements of transient extensional viscosity, performed using the SER fixture in a rotational rheometer.

Monday 5:15 Founders Ballroom B MB14

Extensional flow induced crystallization of polypropylene

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A filament stretching rheometer within a custom build oven is used to impose homogeneous uniaxial flow on linear polypropylene. The Janeschitz-Kriegl protocol is followed and the samples are stretched and allowed to crystallize at a temperature of 146C. Differential Scanning Calorimetry is used to measure the degree of crystallinity of the stretched samples. The flow induced crystallization of the polymer is then characterized as a function of both the total imposed strain and extension rate. We will show that for extension rates corresponding to a Weissenberg number greater than Wi>1, that an increase is observed in the percent crystallinity of the sample reaching a maximum of before decreasing again at high extension rates. Percent crystallinity is observed to increase modestly with increasing strain. Optical polarization microscopy is used to characterize the spherulite size and density and SAXS is used to characterize the crystal size. The increase in crystallinity is likely due to the effective orientation and alignment of the polymer chains with increasing extension rate. Finally, we investigate the crystallization dynamics by investigating the effect of extension rate on the crystallization time by allowing the polymer to crystallize during the stretch. We will show that crystallization time decreases linearly with increasing extension rate.

Symposium MF

Microfluidics, Microrheology and Confined Systems

Organizers: Amy Shen and Pat Spicer

Monday 1:30 Room 204 MF6

Deformation and buckling of colloidal particle stabilized interfaces

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In this talk, the deformation, buckling and folding of particle-laden interfaces will be presented. Colloidal particles can be strongly held at a fluid-fluid interface resulting in an elastic membrane. The deformation of two distinct types of interfaces were explored in this study. The first being an initially spherical particle-laden droplet created using a microfluidic flow focusing device. These droplets were then deformed under nearly uniform extensional flows in a hyperbolic contraction. Additionally, planar particle-laden oil-water interfaces were formed in a Langmuir trough and subjected to a uniaxial compressive strain. When compared to clean water droplets in oil, the deformation of the particle-laden droplet within the microfluidic hyperbolic contraction increased significantly. At large capillary numbers and confinements, the droplets were observed to form two tails and eventually breakup into daughter droplets. Upon breakup, the particle-laden interface on the droplets were observed to buckle and break. These droplets retained their buckled shape far downstream of the contraction. For the interface within the Langmuir trough, compression of the interface was observed to result in buckling and strain localization in the form of folds. The physical properties of the elastic interface were studied, including wavelength and amplitude of the folds as a function of the particle size, polydispersity and interfacial energy and compared to theory.

Monday 1:55 Room 204 MF7

Capillary-driven convective assembly of colloidal monolayers

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We investigate the coupling between the suspension properties and the deposition process during convective deposition of unary suspensions of colloidal silica microspheres. Deposited thin films from this rapid and scalable process have use in a variety of optical, chemical, and biochemical sensing applications. We can direct the formation and ordering of our thin films in order to create multilayer, monolayer, or submonolayer morphologies. Direct measurements of deposition are visualized via high speed confocal laser scanning and scanning electron microscopy in order to generate local dynamic information regarding the deposition as well as the long-range structure of assembled microsphere coatings.

Monday 2:20 Room 204 MF8

Viscoelasticity induced migration of particles in confined flows

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In this work we present novel 3D numerical simulations on the migration of a spherical particle suspended in a viscoelastic fluid under Poiseuille flow. A Giesekus model and a Phan-Thien-Tanner model are chosen as constitutive equations of the suspending liquid. In order to analyze the effect of the fluid viscoelasticity, both fluid and particle inertia are neglected. Viscoelasticity of the suspending fluid induces particle cross-streamline migration. The particle is predicted to migrate either towards channel axis or towards the wall, depending on liquid rheology, geometrical parameters, and its initial position. A neutral cylindrical surface ($r=r^*$) is then found, from which outward motion originates. An instability scenario characterizes the dynamics close to $r=r^*$: when the particle center is at r^*, no transverse motion occurs, but any disturbance in the radial direction triggers the migration. This phenomenology represents the "inversion" of the well-known Segrè-Silberberg effect. Experimental results obtained in a simple micropipe pressure-driven flow confirm the simulation results

Monday 2:45 Room 204 MF9

Microfluidic migration of soft particles in low Reynolds flow

Yeng-Long Chen
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We investigate the concentration profile of soft particles in microfluidic flow due to the competition between shear forces, particle elasticity, particle diffusion, and particle inertia. At low particle Reynolds number ($Re < 1.0$), the soft particles migrate towards the channel center due to the coupling of particle elasticity and wall-induced hydrodynamic interactions. The competition between the shear forces and particle diffusivity, characterized by the Peclet number Pe, is found to affect whether the particles concentrate in the channel center of in an off-center position. As particle Reynolds number increases to moderate values ($Re >\sim 1.0$), the particle concentration profile is found to have two maxima at off-center positions. The migration effect is also found to be enhanced for softer particles with longer elastic relaxation time (higher Weissenberg number). The variation of particle concentration profiles leads to non-linear variations of the mixture viscosity and the average flow rate.

Monday 3:35 Room 204 MF10

Tuning bubbly structures in microchannels

Sharon M. Vuong[1] and Shelley L. Anna[2]
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Foams have many useful applications that arise from the structure and size distribution of the bubbles within them. Microfluidics allows for the rapid formation of uniform bubbles. Bubble size and volume fraction are functions of the input gas pressure, liquid flow rate, and device geometry. The microchannel confines the bubbles and determines the resulting foam structure. We show that bubbly structures can vary from a single row ("dripping" and "slugs"), to multiple rows ("alternating"), to densely packed bubbles ("bamboo" and dry foams). Each configuration arises in a distinct region of the operating space defined by bubble volume and volume fraction. We describe the boundaries between these regions using geometric arguments and show that the boundaries are functions of the channel dimensions. We compare these geometric arguments with foam structures observed in experiments using a flow-focusing design to generate nitrogen bubbles in surfactant-stabilized water. The outcome of this work is a set of design parameters for achieving desired foam structures as a function of device geometry and experimental control parameters.

Monday 4:00 Room 204 MF11

Microfluidics based monodisperse alginate droplet production

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Polymerized alginate microspheres are extremely useful for drug and cell encapsulation due to their nontoxicity and biodegradability. We present a novel way to construct polymerized alginate microspheres using a microfluidic double T-junction system. This microfluidic system exhibits the advantages of in situ polymerization and precise control of particle size. In this system, monodisperse alginate and calcium chloride droplets are created in a single channel in an alternating manner. Due to viscosity differences, a velocity difference is present in the two different droplets inducing coalescence. Following coalescence, the droplets polymerize due to the chemical reaction between alginate and calcium chloride. Through varying the flow rates, flow rate ratio of the two phases, the viscosity ratio of the two phases, and the interfacial tension, the size (diameter ranging from 10 to 300 um) and frequency of the alginate microsphere production is easily controlled. This microfluidics approach can be applied to in situ encapsulation of a variety of cells in monodisperse alginate microspheres for both transplantation and drug delivery applications.

Monday 4:25 Room 204 MF12

Conducting polymer polyaniline droplet production by using microfluidic devices

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Microfluidic devices were developed to produce monodispersed, conducting, responsive polyaniline (PANI) particles for drug delivery and sensor applications. Aniline (Ani) oxidative polymerization using ammonium persulfate (APS) is carried out in a variety of two-phase droplet microfluidic systems. The aniline monomer is contained within the dispersed phase while the oxidizing agent, ammonium persulfate (APS) is contained within the aqueous phase. The production of either solid (aniline, APS in dispersed phase) or shell particles (aniline in dispersed phase, APS in continuous phase) is possible. Droplets are formed by controlling the viscous and capillary forces at the interface. Droplet size is controlled by phase flow rates, the interfacial tension and viscosity ratio between the phases and the inlet geometry. PANI particles are produce via oxidative polymerization. The polymerization is pH dependent and the time of polymerization is monitored by the distance the droplets travel in the channel.

Monday 4:50 Room 204 MF13

Microfluidic synthesis of PDMS beads with tunable stiffness and their application as gas sensors

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Microfluidics is a promising technique for synthesizing monodisperse polymeric microbeads or microgels. To our knowledge, however, this technique has mostly been restricted to creating beads/gels of water-soluble polymers such as alginate or polyethylene glycol (PEG) derivatives. Generation of uniform microbeads of a hydrophobic polymer like polydimethylsiloxane (PDMS) remains an unsolved challenge using microfluidic methods. This is partly because the viscosity of commercial PDMS formulations is high, making it difficult to emulsify them into discrete droplets. Additionally, because of their low surface energy, PDMS microdroplets tend to clump and collapse spontaneously into bigger aggregates. Moreover, microfluidics devices are themselves commonly based on soft lithography using PDMS, which is known to undergo swelling upon contact with a range of solvents. Here we report a novel microfluidic strategy that can address all the above issues. Microfluidic devices are intentionally fabricated using the thermoplasic, poly(methyl methacrylate) (PMMA). The PDMS pre-polymer diluted with a nonvolatile co-solvent is used as the dispersed phase. A planar flow-focusing configuration is used to disperse this phase into droplets by contacting with a continuous phase of water containing an anionic surfactant. Discrete PDMS microdroplets with narrow size distribution are produced thus and collected in a glass vial, where they are subsequently cured thermally into stable microbeads of size ranging from 10 to 200 microns. The stiffness of the beads can be systematically varied by altering the ratio of PDMS pre-polymer to co-solvent. PDMS beads can have a variety of applications. For example, the high permeability of PDMS to most gases allows these beads to be used as gas sensors. To demonstrate this, we have integrated an oxygen-sensitive phosphorescent dye into PDMS beads, and we demonstrate that the resulting beads can function as quantitiative, non-invasive sensors of oxygen in real-time.

Monday 5:15 Room 204 MF14

Hydrodynamic feedback and self-rectification regulate the formation of Newtonian and viscoelastic droplet arrays in a microfluidic network

Swastika S. Bithi and Siva A. Vanapalli
Chemical Engineering, Texas Tech University, Lubbock, TX, United States

We study the dynamics of confined surfactant-laden and surfactant-free drops in a fluidic network containing hydrodynamic traps. When a train of surfactant-coated confined drops is introduced into the network, we find that drops can be trapped at low flow rates due to collective hydrodynamic feedback effects. However, significant polydispersity in the array is observed due to non-uniformity of the droplet size in the train and occasional drop break-up events due to disruption in spacing, driven by non-linear effects at the junctions in the network. In the case of surfactant-free drops, we observe a unique mechanism that generates exceptionally monodisperse microfluidic droplet arrays. Here, we find that when an immobilized drop either under-fills or overfills the trap, subsequent drops rectify its volume through coalescence, followed by break-up. This novel hydrodynamic self-rectification mechanism persists over a broad range of flow rates. We further illustrate the flexibility of this method by generating arrays of viscoelastic polymer fluids. Taken together, the hydrodynamic feedback and self-rectification mechanisms have the potential to array nanoliter volumes of complex fluids for high throughput microrheology and phase behavior studies.

Symposium IR

Industrial Rheology

Organizer: Maryam Sepehr and Hossein Baghdadi

Monday 1:30 Room 207 IR6

Melt extensional viscosity of highly filled thermoplastic blends for automotive heavy layer material

Catheryn L. Jackson[1], James D. Oelberg[2], and James T. Seliskar[2]
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Extensional viscosity is useful for gauging and improving the extrusion and thermoformablility of highly filled thermoplastic blends used in automotive flooring and other applications. The extensional viscosity was measured using the extensional viscosity fixture (EVF) for the ARES Rheometer. Experimental data showing the effect of pre-stretch conditions, rate, temperature and other variables for different formulations will be presented. Extensional viscosity data will also be related to extrusion and thermoformability.

Monday 1:55 Room 207 IR7

Extensional rheometry of aqueous PZT ceramic slips

Saumil S. Vadodaria[1], Rob English[1], Gavin Buckles[2], and Tom Dobbie[3]
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Many technical ceramics, such as lead zirconate titanate (PZT), are processed via spray drying, a process in which a fluid aqueous slip stabilised by a polymeric dispersant is atomised and de-watered to produce a granular powder. It is essential to maintain control over the particle size distribution and morphology of the granules, as these properties directly influence downstream process ability (compression moulding), bulk density in the green state and final application (piezoelectric) properties of the ceramic. Atomisation of the slip is dominated by the extensional flow of the fluid. Measurement of the extensional viscosity of low viscosity fluids of high specific gravity is non-trivial and hence presents experimental challenges. The present study compared a number of experimental approaches suited to the estimation of the extensional viscosity of PZT ceramic slip formulations. These included a confined flow through an abrupt contraction using a capillary rheometer, with data treatment based on the method of Cogswell. Comparative measurements using a planar hyperbolic slot die were also performed, in addition to free surface measurements based on capillary breakup (CaBER). A critical overview of the relative merits of each technique is then presented. The effect of dispersant concentration on viscosity was also determined. The viscosity was found to be a function of the polymer adsorbed on the ceramic particles and the amount of polymer present in the continuous phase. In simplistic terms, increasing the extensional viscosity of the slip acts to suppress the break-up of the fluid (Usually dominated by surface tension). This generally results in the generation of larger droplets and subsequently granules of larger size. In this respect, reliable extensional measurements offer a significant advancement and remarkable potential as a formulation tool. The control of slip rheology and stability through the use of functional polymers and the influence on the extensional viscosity is demonstrated.

Monday 2:20 Room 207 IR8

Annular displacement flows in the cementing of oil and gas wells

Mariana Carrasco-Teja and Ian A. Frigaard
Mathematics, University of British Columbia, Vancouver, BC V6T1Z2, Canada

We study the displacement of one Bingham fluid by another in a nearly horizontal narrow annuli where the inner cylinder is rotating and reciprocating slowly. The main application is the primary cementing of horizontal oil and gas wells, where drilling mud must be completely displaced from the annulus with cement and other intermediate fluids. Primary cementing is a crucial step in the construction of a well as it provides zonal isolation of the reservoir from the surface. Poorly performed cementing operations can lead to both environmental and safety problems, e.g., as shown spectacularly in BP's Deepwater Horizon incident. In the well cementing industry it is widely believed that rotation and reciprocation of the casing leads to a better displacement of the drilling mud. Using a Hele-Shaw modelling approach, we simulate the displacement process and explore the effects of using yield stress fluid combined with a moving casing. Industrial intuition is not always confirmed.

Monday 2:45 Room 207 IR9

Exponential shear of downhole fluids

Jason Maxey and Ryan van Zanten
Baroid Research & Development, Halliburton, Houston, TX 77032, United States

Exponential shear has been explored as a method to produce strong flows similar to those experienced in planar and uniaxial elongation. Significant work has been done to examine dilute polymer solutions through this methodology. Arguments continue over whether exponential shear actually produces a strong flow, though there is general agreement that the degree of chain stretching induced by exponential flows does not approach that experienced in elongational flows. There has been little work done, however, in examining the behavior of colloidal suspensions under exponential shear.

Downhole fluids for oilfield drilling, completion, and fracturing utilize polymers, biopolymers, clays, emulsions, and suspensions of colloidal particles in near-saturated brines or oils (iso-olefins, esters, paraffins, etc.). In normal drilling and completion operations there are multiple areas where elongational flows are experienced, such as when the fluid passes through the bit or is forced into porous formations. The elongational behavior of the fluid can determine such things as the rate of fluid invasion into formations, the ability of the fluid to form an effective filter cake, and the potential for formation damage from fluid invasion which leads to blockage of the reservoir pore spaces and reduced hydrocarbon production.

In this work exponential shear is utilized to study a variety of downhole fluids. Exponential shear material functions are compared to standard oilfield tests for high-temperature / high-pressure fluid loss and the potential for formation damage, as well as to standard shear rheology.

Monday 3:35 Room 207 IR10

Rheological characterization of waxy crude oils

Flávio H. Marchesini[1], Alexandra A. Alicke[1], Paulo R. de Souza Mendes[1], and Cláudio Zíglio[2]
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Along the last decades a great amount of effort has been devoted to develop a reliable methodology for measuring rheological properties of different waxy oils, aiming at understanding the effects of the cooling and shearing history on rheological properties such as viscosity, yield stress, storage and loss moduli. In this talk we present a fairly complete rheological characterization of waxy crude oils, including temperature ramps, flow curves, constant stress and stress-amplitude-sweep tests, and compare the results obtained with the ones found in the literature. It is observed that additional precautions must be taken to ensure the production of reliable data for waxy oils from rotational rheometry. We highlight the effects of holding time and of temperature and shear histories on the microstructure, and consequently on the postcooling rheological properties of these oils.

Monday 4:00 Room 207 IR11

Viscosity evaluation of mixtures of biodiesel

Fernando Luiz B. Abreu[1] and Dalni M. Santo Filho[2]
[1]Coordenação de Pesquisa e Pós-graduação, Instituto Federal do Rio de Janeiro, Paracambi, Rio de Janeiro 26600000, Brazil; [2]Laflu, Inmetro, Rio de Janeiro, Brazil

Rheometers are devices know to be versatile since it can measure both newtonian and non-newtonian fluids. It is, however, not yet clear how to evaluate the measurement uncertainty of such devices, despite their development, which has made them more automatic and versatile, enabling the user to adjust the equipment accordingly with the many quantities involved (such as reference oil viscosity, temperature, angular velocity, etc) and the many measurement systems involved (cone and plate, parallel plate and concentric cylinders) all the while observing the fluids flow. In this work, percentages of B-100 biodiesel, both from soy and beef tallow, were studied. Two methodologies were created with the purpose of finding the dynamic viscosity of the studied oils and to compare the encountered results. In the first, the dynamic viscosity will be calculated by comparing a capillary viscometer and a digital densimeter, both national standards of the INMETRO (National Institute for

Metrology, Normalization and Industrial Quality of Brazil) and in the second, the dynamic viscosity will be obtained directly from the rheometer. The results from both approaches will be compared using the relative error.

Monday 4:25 Room 207 IR12

Applied rheology in decorative and protective coatings

Richard R. Eley
Akzo Nobel Coatings, Strongsville, OH 44136, United States

Architectural and industrial coatings are among many rheologically complex fluids whose commercial viability depends on tailoring the rheology to the end use. For such materials, the stresses and strain rates involved in processing and application must be considered when defining the necessary rheological properties. The aim of industrial applied rheology is to predict and improve fitness-for-use of fluids of commerce from fundamental properties. The coatings industry (and many others) typically relies on simple viscometers or "viscometry devices" for quality control and product development. These devices measure within a limited range of stress or strain rate, generally returning arbitrary numbers of demonstrably limited value. It is also true, however, that a robust link between fundamental rheological properties and "real-world" coatings performance has proven difficult to establish. The conundrum for the applied rheologist is how to design experiments that are relevant to the process at hand, and then usefully apply the result - in other words, to bridge rheology and technology. In this paper, methods of rheological characterization of coatings that we have found useful for evaluation and prediction of performance will be discussed. In particular, the value of the shear stress as the independent variable in understanding coating flows will be brought out, via a flow curve "stress-mapping" technique. Such results can be directly related to application and film formation processes. The relationship of microstructure to flow curve shape will be discussed. Finally, examples of the direct application of rheological data in the computer simulation of coatings flows will be given.

Monday 4:50 Room 207 IR13

High-throughput rheology using robotic systems

Suraj S. Deshmukh, Matt Bishop, Jodi Mecca, Dan Dermody, Eddie Gee, Jon Zieman, Brian Orvosh, and TC Kuo
Core R&D, The Dow Chemical Company, Midland, MI 48674, United States

Rheological characterization is a crucial screen for gauging the performance of a wide range of commercial products including paints, water soluble polymers, shampoos etc. Measurement of simple rheological functions such as viscosity and complex rheological properties such as elasticity and LAOS functions have traditionally been a labor intensive and tedious task for researchers. The Rheology workflow is a scientific process starting from design of experiments to formulation to rheological characterization and finally data analysis. In our work, we have endeavored to remove the bottlenecks in this scientific process making this is a rapid, efficient and fairly accurate High Throughput Rheology workflow. A number of tools that are part of this workflow have been developed over the past few years including some of the world's first high throughput rheometers and viscometers. I will outline the development of a novel high throughput viscometer which in conjunction with an automated cone and plate rheometer that includes automated sample handling, loading and cleaning systems make this an efficient screening and measurement process. Further, validation of these instruments will be described including systematic experimental observations and model simulated results which were used to identify optimum operating and test conditions. Also, rapid data visualization tools while maintaining the analysis in the hands of the experienced experimentalist will be outlined.

Monday 5:15 Room 207 IR14

A new apparatus for powder flow testing: A different type of rheometry

David J. Moonay
Brookfield Engineering Laboratories, Inc., Middleboro, MA 02346, United States

Bulk solids flow is commercially or industrially important. Dispensation of solids, particularly after consolidation during storage over various time periods, may be problematic. The "field fixes" often result in damaged equipment. Problems range from significant feed difficulties in various processes to catastrophic silo failures. Existing test methods are often crude, providing information that often does not appreciably help. Poor predictive value may result in improper hopper design. Some instruments, although providing better data, are prohibitively large and expensive. Bulk solids flow is typically dominated by yield behavior and greatly affected by compaction. Using basic principles and drawing upon experience, a new, conveniently-sized, affordable, easier-to-use, highly-automated instrument was developed. The Brookfield Powder Flow Tester(tm) and associated Powder Flow Pro(tm) software are used together to test myriad powders, up to approximately 1.5 mm in diameter. The basic design, operating principles and results from testing various materials will be presented. A powdered detergent, for example, was analyzed in multiple sample runs. Some of the calculated average values, from wall friction tests, include: maximum wall angle, 26.3° ± 0.3°; maximum wall cohesion, 0.376 ± 0.023 kPa; and the friction angle, 28.0° ± 1.3°. Flow function test results will also be presented and discussed; results include bulk density as a function of consolidation stresses, for example. This instrument is already proving useful in testing products ranging from powdered foods to finely-ground minerals.

Tuesday Morning

Symposium PL

Plenary Lectures

Bingham Lecture

Tuesday 8:30 Amphitheater A/B PL2

The local and non-local rheology of vesicle and capsule suspensions

Eric S. Shaqfeh
Chemical Engineering, Mechanical Engineering, ICME, Stanford University, Stanford, CA 94305, United States

It is well known that individual vesicles or liposomes (i.e. fluid enclosed by a lipid bilayer membrane suspended in a second fluid) are characterized by a remarkable dynamics in flow. For vesicles that are "near spheres" this dynamics includes at least 5 different types of orbits in shear flow that are functions of the viscosity ratio between the inner and outer fluid as well as the Capillary number based on the bending modulus. However, this dynamics becomes even more rich as the reduced volume falls below about 0.65 where now there are atleast three equilibrium shapes (prolates, discocytes, and stomatocytes) which are linearly stable. These each are characterized by their own flow dynamics -- including transitions among the different shapes! It is therefore not surprising that a suspension of vesicles is characterized by fascinating collective behavior as well. I will discuss our recent development of a numerical code (based on Loop subdivision) which allows the Stokes flow simulation of non-dilute suspensions of vesicles and capsules at essentially any value of the reduced volume. We will then use these numerical simulations to examine the local and nonlocal (or micro-) rheology of vesicle and capsule suspensions ultimately relating the rheology to platelet margination in the microcirculation.

Symposium SG

Rheology of Solids, Glasses and Composites

Organizers: Daniel J. Lacks and Sadhan C. Jana

Tuesday 10:00 Amphitheater A SG1

A simple molecular constitutive model that predicts yielding and strain hardening in extensional flow of polymer glasses

Suzanne M. Fielding[1], Ronald G. Larson[2], and Mike Cates[3]
[1]Physics, Durham University, Durham, United Kingdom; [2]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States; [3]Department of Physics, The University of Edinburgh, Edinburgh, Scotland EH9 3JZ, United Kingdom

Strain hardening has long been an observed feature of polymer glasses in extension; explanations to date have often been phenomenological. Ediger and coworkers (Lee et al. Science 323, 231, 2009) have recently shown in experiments on PMMA glasses that, in addition to strain hardening, polymeric glasses show a remarkable non-monotonicity in the segmental relaxation time both in loading and unloading of stress. Here, we develop a simple constitutive equation for polymer glasses that uses ideas from recent theories for yielding in simple glasses (Brader et al. PNAS, 106, 15186, 2009) to represent local segmental modes in the polymer, and combines a simple model for this with an elastic dumbbell model for the slow rubbery polymer relaxation modes. This simple constitutive model shows that the remarkable features of polymer glasses seen in the work of Ediger and coworkers are a consequence of the combination of stress-induced liquefaction of the segmental modes, with a rubbery polymer entropic stress. For a polymer glass under uniaxial loading, the model predicts that the liquefaction of the segmental modes permits rubbery strain hardening of the polymer modes to emerge, and once this emerges, it slows the deformation of the material under constant load enough to partially re-vitrify the segmental modes even though they remain under stress. In this way, the observed non-monotonicity in the segmental relaxation modes is produced, both on loading and on unloading. Our theory suggests that such behavior should be universal in polymer glasses, but that the details can be modified, for example, by augmenting the modulus of the segmental mode relative to the rubbery mode, either by stiffening the polymer, or by adding molecule additives. Thus, our simple model is qualitatively consistent with experimental data of Ediger and coworkers, and can be tested and exploited by varying polymer stiffness, molecular weight, and the presence of small-molecule additives. It can also be applied to shear and other flows.

Tuesday 10:25 Amphitheater A SG2

On rheology, cure kinetics and chemorheology of gum rubbers

Arpita Mitra[1] and Arkadii I. Leonov[2]
[1]Corning Incorporated, Corning, NY 14830, United States; [2]Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301, United States

The paper presents an experimentally supported modeling approach, which describes the rheology, detailed cure kinetics, and chemorheology of a gum elastomer in course of sulfur accelerated vulcanization. Changes in the rheology during cure reaction are correlated with degree of cross-linking, described by vulcanization kinetics. Oil extended SBR exemplifies the approach.

Tuesday 10:50 Amphitheater A SG3

Predicting the rheology of long glass fiber reinforced thermoplastic melts in a simple shear flow

Kevin C. Ortman and Donald G. Baird
Chemical Engineering, Virginia Tech, Blacksburg, VA, United States

It is desirable to understand the link between the rheological response of a long glass fiber (> 1 mm) reinforced thermoplastic melt and its underlying microstructure. Specifically, we are interested in associating the rheological behavior of long glass fiber reinforced polypropylene with the transient evolution of fiber orientation, in simple shear flow, to ultimately model fiber orientation in complex processing flows. A sliding plate rheometer was designed to measure stress growth at the startup and cessation of steady shear flow. A modified form of the Lipscomb stress tensor is presented and is used in combination with a semi flexible orientation model to describe the rheological response of the long fiber systems.

Tuesday 11:15 Amphitheater A SG4

Modeling environmentally induced changes in elastomer modulus

Christopher C. White, Don Hunston, and Kar Tean Tan
Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States

A major scientific goal for the last 100 years has been the effective modeling of changes in material properties induced by exposure to outdoor environmental exposure. Monitoring changes to the stress relaxation modulus of a filled elastomer enables the impact exposure to elements of the weather to be determined. This is significant issues as filled elastomers, a $50B/yr industry are responsible for differentiating the conditioned inside space from the outside. Over 74% of the electricity in the US is consumed conditioning the space inside buildings. At some point, those sealants/elastomers fail to seal the building resulting in significant energy loss and moisture intrusion. An accurate predictive model of failure for organic materials exposed to weathering has eluded the scientific community for over 100 years. In building an accurate predictive model of filled elastomer behavior two important challenges presented: The elastomer exhibits strain dependant non-linear viscoelastic behavior including the Mullins effect. Significant effort must be spent ensuring that any measured changes to the stress relaxation modulus are causally related to the exposure conditions and not changes to the characterization of the elastomer. These efforts will be examined. The second major concern is establishing which elements of the outdoor environmental exposure are responsible for the majority of the changes to the stress relaxation modulus. This work has focused on establishing four elements of the weather as statistically significant: temperature, humidity, ultra violet radiation and mechanical loading. Statistical findings are presented that establish these four elements of the weather as significant factors in the modulus change of exposed filled elastomers.

Tuesday 11:50 Amphitheater A SG5

Soft-particle suspensions near jamming: Effective diffusion

Craig E. Maloney, Peter Trocha, and Kamran Karimi
Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Suspensions of soft particles exhibit a remarkable bifurcation at the random close packing volume fraction, f_c [1]. There is a yield stress at vanishing shearing rate above f_c but not below. We perform numerical simulations of soft-particle suspensions under shear near f_c. We find that above f_c at sufficiently low shearing rates, the effective diffusion constant, D_{eff}, scales with length of the simulation cell in the flow-gradient direction. This is in agreement with the size-dependent diffusion constant observed in low-temperature Lennard-Jones glasses. Furthermore, the value of D_{eff} can be understood in terms of organized lines of slip and is independent of the form of the repulsive interactions between the particles and the precise way in which the viscous drag of the suspending fluid is modeled in the particle-scale simulations.

[1] Microfluidic Rheology of Soft Colloids above and below Jamming. K. N. Nordstrom, E. Verneuil, P. E. Arratia, A. Basu, Z. Zhang, A. G. Yodh, J. P. Gollub, and D. J. Durian. Phys. Rev. Lett. 105, 175701 (2010) - Published October 21, 2010

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Tuesday 10:00 Amphitheater B SC15

Physical origin of shear-banding in jammed systems: A toy model

Philippe Coussot and Guillaume Ovarlez
Laboratoire Navier, Université Paris-Est, Champs sur Marne 77420, France

A wide range of materials (concentrated emulsions, foams, colloids, etc) are considered as jammed systems but they have very different types of structures at a local scale so that the unity of these systems mainly relies on their (macroscopic) mechanical properties. Their basic, common, rheological property is their yield stress, namely the fact that they can flow only when submitted to a stress larger than a critical value. Recently it was suggested that attractive (jammed) systems would tend to develop shear-banding (coexistence of sheared and unsheared regions at sufficiently low apparent shear rates even in homogeneous stress field) whereas repulsive systems would not [Becu et al., Phys. Rev. Lett. (2006), Ragouilliaux et al., Phys. Rev. E (2007), Rogers et al., Phys. Rev. Lett. (2008)]. Besides, different types of models were able to predict the possibility of shear-banding for an appropriate set of unphysical parameters in purely phenomenological and mesoscopic approaches, i.e. "Lambda model", "SGR model" or "Fluidity model". In order to rationalize existing data concerning the flow characteristics of jammed systems and in particular understand the physical origin of such a difference we propose a simple approach (a "Toy model") [Coussot-Ovarlez, Eur. Phys. J. E (2010)] for describing the steady flow behaviour of yield stress fluids, which retains only basic physical ingredients. Within this framework we show that in the liquid regime the behaviour of jammed systems turns from that of a simple yield stress fluid (exhibiting homogeneous flows) to a shear-banding material when the ratio of a characteristic relaxation time of the system to a restructuring time becomes smaller than 1, thus suggesting a possible physical origin of these trends. We show that this result is qualitatively in agreement with existing data and in quantitative agreement with a new set of "local" rheological data obtained by MRI for a colloidal suspension.

Tuesday 10:25 Amphitheater B SC16

Microstructure measurements of shearing concentrated, near hard sphere colloidal dispersions via 1-2 plane flow-SANS

Norman J. Wagner, Dennis Kalman, and Lionel Porcar
Chemical Engineering, University of Delaware, Newark, DE 19716, United States

Concentrated colloidal suspensions of hard, spherical particles exhibit shear thinning, shear thickening, and normal stress differences due to flow-induced microstructural rearrangements. This presentation presents the first direct measurements of these microstructural rearrangements measured in the plane of flow (1-2 plane). We develop a new experimental flow-SANS cell suitable for Small Angle Neutron Scattering Measurements (SANS) in the plane of flow (1-2 plane) and combine that with rheo-SANS in the radial direction (1,3 plane) to elucidate the connection between the microstructure and the measured shear rheology. Significant anisotropic structural rearrangements under shear are evident in the 1-2 plane. These microstructure changes are compared to the rheological behavior via stress-SANS laws that separate the thermodynamic and hydrodynamic components of the stress that drive shear thinning, shear thickening, and first normal stress differences. The experimental results are compared against predictions of Stokesian Dynamics simulations and theory.

Tuesday 10:50 Amphitheater B SC17

Normal stress distribution in highly concentrated suspensions undergoing squeeze flow

Mohsen Nikkhoo, LeAnne Brozovsky, Khosrow Khodabandehlou, and Francis A. Gadala-Maria
Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, United States

Using pressure-sensitive films we measured the normal stress distribution in highly concentrated suspensions of glass beads in a Newtonian fluid undergoing squeeze flow with a constant force between two parallel circular disks. To our knowledge these are the first reported measurements of this kind. At low concentrations, the normal stress distribution is parabolic, with a maximum at the center, as predicted for pure Newtonian fluids. This distribution persists for moderate concentrations. However, beyond a critical concentration, the normal stress distribution becomes drastically different from that for Newtonian fluids, exhibiting normal stresses an order of magnitude larger near the center and very low normal stresses beyond that region. The central region of high normal stresses seems due to a significant accumulation of particles in that region. There is almost no slip in the central region and considerable slip beyond that. At high concentrations, changes in the normal stress distribution during the squeezing process were ascertained by stopping the experiment, changing the pressure sensitive film, and then resuming the experiment. These tests indicate that the normal stresses in the outer regions of the disk decrease as the squeezing proceeds.

Tuesday 11:15 Amphitheater B SC18

Percolation, structure, kinetic arrest, and mechanical response in dense mixtures of rods and nanospheres

Ryan B. Jadrich[1] and Kenneth S. Schweizer[2]
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Conductive ink gels composed of mixtures of rod-like and spherical metallic nanoparticles find use as printable electrodes for fragile electronic devices and solar microcells. More generally, binary rod-sphere systems are of broad interest in soft materials engineering and diverse biological contexts. We have developed and applied several microscopic statistical mechanical methods to study the real space structure, connectivity, and slow dynamics of such mixtures. Integral equation theory has been extended to treat the continuum percolation of rods and spheres. Rod addition to a spherical particle fluid significantly enhances the connectivity in a manner that depends on composition, rod aspect ratio, and interparticle attraction strength. The center-of-mass version of Naïve Mode Coupling theory (NMCT) has been generalized to treat rod-sphere mixtures, and predicts the emergence of a remarkably large number of kinetically arrested states. For example, for a high total packing fraction matched diameter attractive rod-sphere mixture, up to seven dynamical phases occur involving full or partial localization into a repulsive glass, attractive glass, gel, or a mixed coexisting "glass-gel" state. This complexity reflects the subtle interplay of repulsive forces (caging), attractive forces (bond formation), and steric packing asymmetry. Removal of nanosphere attraction destroys the double gel state but otherwise has minor consequences. Elastic shear modulus calculations reveal that rods store significantly more stress than spheres due to their shorter localization length, and the modulus can undergo orders of magnitude change upon crossing dynamic phase boundaries. As the strength of attraction between all species in the mixture grows, the elastic modulus becomes less sensitive to composition due structural reorganization. Finally, mechanically-driven yielding has been studied, and correlated with the nature of the kinetically arrested phase and its quiescent shear modulus.

Tuesday 11:50 Amphitheater B SC19

Rheology and micro-structure of concentrated non-Brownian suspensions

Frédéric Blanc, François Peters, and Elisabeth Lemaire
LPMC, UNS- CNRS, Nice 06108, France

Concentrated suspensions are very common in several engineering fields or geophysical. Thus, it is of importance to understand their mechanical behaviour but this is a hard task since there exists a strong coupling between the flow and the microstructure of the suspension. Indeed, under the effect of the flow, the particles do not remain homogeneously dispersed in the suspension. The flow is responsible for the development of heterogeneities: at the particle scale transitory aggregates appear and at the flow scale, it is usual to observe that the particle concentration is not constant. These heterogeneities partially invalidate the results of macroscopic rheological measurements and require to perform local measurements. To this aim, we have mounted an experiment where the velocity and particle concentration profiles are measured thanks to Particle Image Velocimetry (PIV) or Particle Tracking Velocimetry (PTV). The suspension is sheared in a cylindrical wide gap Couette cell. A laser sheet, in the plane perpendicular to the cylinders axes, illuminates the suspension and a camera situated under the Couette cell registers the suspension images at different times. The refractive indices of the particles and of the fluid are close enough together for the suspension to be transparent, even for concentrations as high as 50%. The transient response under shear reversal is studied for various particle concentrations comprised between 25 and 55%. During the shear reversal, both the local viscosity, deduced from the measurement of the velocity field, and the pair correlation function are recorded. After shear reversal, the viscosity undergoes a step-like reduction, decreases slower and passes through a minimum before increasing again to reach a plateau. The pair correlation function for shear in one direction is observed to be the mirror image of that obtained for shear in the opposite direction. When the viscosity passes through the minimum, the pair correlation function is observed to be almost symmetric.

Symposium MF

Microfluidics, Microrheology and Confined Systems

Organizers: Amy Shen and Pat Spicer

Tuesday 10:00 Room 204 MF15

High-throughput rheology using a microfluidic device

Eric M. Furst and Kelly M. Schultz
Department of Chemical Engineering, University of Delaware, Newark, DE 19716, United States

Engineered soft materials are frequently composed of many components that can interact in complex and potentially unintended ways. This makes the prediction and control of properties such as the phase behavior, microstructure and rheology of these materials difficult, and impacts diverse applications that range from consumer care products to hydrogels for regenerative medicine. It is desirable to have effective and efficient high-throughput methods to screen material properties over a large composition space, while minimizing the time and cost of such measurements. In particular, this enables the characterization of emerging materials that are expensive, hard to procure or difficult to synthesize.

In this talk, we will present high-throughput rheological measurements using a microfluidic device. A series of microrheology samples is generated as droplets in an immiscible spacer fluid using a microfluidic T-junction. The compositions of the sample droplets are continuously

varied over a wide range. Rheology measurements are made in each droplet using multiple particle tracking microrheology. We will discuss the critical design and operating parameters, including the droplet size, flow rates and rapid fabrication methods and validation experiments. Overall, the combination of microrheology with microfluidics maximizes the number of rheological measurements while simultaneously minimizing the sample preparation time and amount of material, and should be particularly suited to the characterization of scarce and complex soft materials.

Tuesday 10:25 Room 204 MF16

Quantification of the interfacial rheology of a model oil-brine-dispersant system at microscale interfaces

Matthew D. Reichert[1], Nicolas J. Alvarez[1], Shelley L. Anna[2], and Lynn M. Walker[1]
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In the recent Gulf of Mexico oil spill, nearly two million gallons of dispersants were sprayed both at the surface and 1.5 kilometers below the surface in order to disperse leaking oil. Many decisions on application were made without detailed knowledge of the efficacy of these dispersants in differing environments. At the well head, the temperature of the oil is significantly higher than temperatures for typical dispersant application and the process involves flow conditions previously unexplored for dispersant application. In this work, we quantify the interfacial tension dynamics and rheology of a model oil-water-surfactant (squalane-brine-Tween-80) system, to characterize how the influence of interface curvature, flow conditions, and temperature impact fundamental surfactant transport. Our goal is to use this information to inform decisions in the dispersion process. Using a recently-developed microtensiometer, interfacial tension dynamics and interfacial rheology measurements are performed on curved interfaces approaching 30 microns in radius, over a wide temperature range. The advantage of using microscale interfaces is rapid measurement and the ability to control the local environment. We are able to exchange one of the fluids near an oil-water interface to use convection to shift transport regimes and also to investigate situations such as step changes in bulk concentration on the interfacial properties. Results on the interfacial properties (equilibrium and dynamic) and interfacial rheology of these interfaces will be presented and discussed in the context of dispersant design.

Tuesday 10:50 Room 204 MF17

Polymer melt microfluidics: Rheology, mixing, and compatibilization and interfacial tension

Kalman B. Migler and Doyoung Moon
Polymers Division, NIST, Gaithersburg, MD 20850, United States

We describe our progress towards the development of an integrated micro-fluidic platform for the measurement of fundamental polymer melt properties and fundamental processing operations. We emphasize that our use of pressure driven flow through easily reconfigurable metal shims provides for a diversity of operations that typically require distinct rheometers, mixers and extruders. We conduct rheological measurements by tracking the flow front through a simple channel. We conduct mixing and compatibilization by flow through serpentine split and recombine mixers, followed by post-experiment electron and CARS microscopy. Finally, we demonstrate that the platform can be used for interfacial tension measurements, by utilization of flow focusing to create droplets, utilizing pressure driven flow to distort them and then monitoring their relaxation back to a spherical shape. The advantages of this approach include minimal handling of the material, the ability to simultaneously measure viscosity and the ability to manipulate the interface in real time.

Tuesday 11:15 Room 204 MF18

Multiplexed microfluidic viscometer for complex fluid and blood rheology

Deepak E. Solomon and Siva A. Vanapalli
Chemical Engineering, Texas Tech University, Lubbock, TX, United States

Recent advances in microfluidics have enabled viscometers to be fabricated from microfluidic devices. The potential benefits of these microfluidic viscometers include operation with small sample volumes ranging from nanoliters to microliters and access to shear rates not achievable by conventional rheometry. For biological fluids such as blood, the microfluidic format also enables measurements to be made in conditions mimicking blood flow in microvessels. Finally, the microfluidic viscometers have the potential to be multiplexed for high throughput analysis.

In this work, we operate the viscometer using two co-flowing miscible laminar streams - one of which is the test fluid and the other is the reference fluid. By measuring the width of one of the streams and knowing the flow rates of both streams and viscosity of the reference fluid we are able to extract the viscosity of the test fluid. We operate the device in two modes - interface displacement and interface compensation. Both techniques show good agreement with results obtained from a conventional rheometer for Newtonian liquids, polymeric fluids and red blood cell suspensions. We also characterize the sensitivity and limits of operation of this device. By exploiting the interface displacement technique, we develop a multiplexed version of this device that allows simultaneous viscosity measurements on four different fluids. We further use the multiplexed device for investigating the role of channel confinement on the viscosity of red blood cell suspensions.

Tuesday 11:50 Room 204 MF19

Intracellular particle-transport as a measure for cancer-cell aggressiveness

Naama Gal and Daphne Weihs
Biomedical Engineering, Technion-Israel Institute of Technology, Haifa, Israel

Mechanical properties of cells have been of increasing interest over the last few years. Many works use real-time motion or probe particles within living cells as a measure for their mechanics. Motion of those particles provides an indication of the local intracellular structural-density and active transport processes. However, the correlation between structure, mechanics, activity, and especially local rheology is still unclear in those systems. Cells regulate internal mechanics over short time scales for crawling and division, as well as for intracellular transport. In parallel, cell structure and stiffness play a role in cancer, where flexible cells may invade the body to initiate a secondary tumor.

In this work, we evaluate the internal mechanics of three closely related model breast-cancer cells with varying aggressiveness and introduce new trajectory analysis approaches. Particle motion is evaluated using measures such as displacements, velocities, trajectory radius-of-gyration, relative location in the cell, and others. Interiors of the aggressive cancer cells were softer and more active than the benign cells and low-aggressiveness cancer cells. We explain differences in intracellular mechanics as measured by particle motion in terms of cancer aggressiveness, cell activity, and cell structure.

Symposium CR

Computational Rheology

Organizers: Randy Schunk and Juan P. Hernandez-Ortiz

Tuesday 10:00 Room 207 CR1

Molecular dynamics simulations of flow-mediated interactions between cylindrical micelles

Ashish V. Sangwai and Radhakrishna Sureshkumar
Syracuse University, Syracuse, NY, United States

Cylindrical micelles in solution, when subjected to shear or elongational flow, can self-assemble to form flow-induced structures (FIS) even below the overlap concentration. This effect is especially prominent in the presence of added salts with counterions such as salicylate that strongly bind with the micelle surface. At low shear rates, the solutions show no apparent change in viscosity as a function of shear rate; however, a non-linear increase in viscosity is observed above a critical shear rate accompanied by the formation of a gel-like phase. This is attributed to the increase in the linear dimension of cylindrical micelles due to their flow alignment and collision to form large polymer-like aggregates. A comprehensive theoretical model for the formation of FIS has been provided by Turner and Cates [J. Phys. Condens. Matter, 4, 3719 (1992)]. In this work, we investigate the flow dynamics of cylindrical micelles of cetyltrimethylammonium chloride (CTAC) surfactant in the presence of sodium salicylate salt modeled with previously benchmarked coarse-grained potentials from the MARTINI force field with non-equilibrium molecular dynamics (NEMD) simulations [A.V. Sangwai & R. Sureshkumar, Langmuir, DOI: 10.1021/la2006315]. Micelle dynamics are studied as a function of the shear/elongation rate or equivalently the Peclet number, Pe. Flow-alignment is observed at O(1) values of Pe. For Pe >> 1, the micelle is found to break under flow-induced stresses. In another set of NEMD simulations, flow-mediated binary interactions between cylindrical micelles are studied. It is shown that for O(1) Pe, collision of flow-aligned micelles can break their end-caps, resulting in the merger of the two micelles to form a longer single cylindrical micelle. To our knowledge, this is the first molecular-level evidence in support of the mechanism proposed by Turner and Cates.

Tuesday 10:25 Room 207 CR2

Dynamic arrest and creep in a simulated associative polymer gel

Arlette R. Baljon[1], Joris Billen[1], Adam Coleman[1], and Rajesh Khare[2]
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At low temperatures the viscosity of an associative polymer melt diverges due to the formation of extremely long-lived aggregates. We explore this so-called "jammed" state in a hybrid molecular dynamics/Monte Carlo (MD/MC) computer simulation of telechelic polymers[1], in which temporary bonds between chain end-groups form and break during the course of the simulation. Two phenomena will be discussed. First, we investigate the extent to which dynamic arrest occurs due to percolation. Since clusters of chains spanning the system are found even at temperatures at which everything flows smoothly, the occurrence of percolation at one moment in time is not enough. Our focus is thus on determining if a percolating network, consisting only of bonds with very long lifetimes, "jams" the system. Second, we investigate the behavior of the jammed system under a small stress. Below a critical stress, slow creep is observed. The shear rate exhibits both positive and negative values with the mean being positive. These athermal nonequilibrium fluctuations obey the Gallavotti-Cohen steady-state fluctuation theorem. This allows us to calculate the effective temperature that characterizes the fluctuations. These nonequilibrium fluctuations might be a general property of a jammed state. They are also observed in other systems driven far from equilibrium, such as wormlike micelles[2]. The fluctuation theorem expresses the fluctuations in terms of rates of entropy production and release. A negative shear rate is due to a temporary decrease in entropy and increase in elastic properties. We will report on the underlying microscopic changes in the polymer network structure, which cause the fluctuations in the shear rate.

1. Baljon et al., J. Chem. Phys. 126, 044907 (2007). 2. Majumdar et al., Phys. Rev. Lett. 101, 078301 (2008).

Tuesday 10:50 Room 207 CR3

Particle rheology simulations of viscoelastic properties

Mir Karim and Rajesh Khare

Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States

The viscoelastic properties of complex fluids are governed by their molecular structure. Molecular simulations provide the ability for explicit treatment of this detailed molecular structure as well as the specific chemical interactions in the system. The focus of our work is on the determination of the local viscoelastic properties of polymeric systems using a simulation approach that is similar to the particle microrheology technique that is now widely used for the experimental determination of the mechanical properties of complex fluids. The simulation system will consist of a probe particle that is embedded in a polymer melt. The polymer chains will be represented using bead-spring models and the probe particle motion in the matrices of interest will be studied using molecular dynamics simulations. Analogous to the particle microrheology techniques, the mechanical properties of the medium will be determined by the analysis of the probe particle motion. Both active and passive particle rheology approaches will be employed in our simulations. We will present a quantitative comparison of the viscoelastic property values obtained using these two particle rheology approaches, and also compare these values with those calculated using approaches similar to the bulk rheology techniques. Results will also be presented for the effects of chain length and chain topology on the viscoelastic properties.

Tuesday 11:15 Room 207 CR4

Concentration dependent dynamics of polymer solutions: Universal behaviour from coarse-grained simulations

A. Jain[1], P. Sunthar[2], B. Duenweg[3], and J. R. Prakash[1]

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Many important phenomena in both industrial and biological contexts involve polymer solutions in the semi-dilute solution domain. However, the behaviour of polymer solutions is presently well understood only in the dilute and concentrated solution limits. Computational prediction of the static and dynamic properties of semidilute polymer solutions requires the simulation of a large system of polymer chains interacting with each other through many-body interactions, including excluded volume and hydrodynamic interactions. While excluded volume interactions are short-ranged in space, hydrodynamic interactions are long-ranged. We describe the development of a Brownian dynamics simulation algorithm that uses a fast implementation of the Ewald summation method. Measurements have been carried out to examine the influence of several tuning parameters involved in the Ewald summation. A set of values is suggested for these parameters to obtain fast and efficient simulations. Green-Kubo auto correlation functions are used to obtain predictions of the concentration dependence of static properties such as the radius of gyration, and of dynamic properties such as the long-time diffusivity and the zero shear rate viscosity. Simulation results are compared with the experimental observations on semi-dilute DNA solutions.

Tuesday 11:50 Room 207 CR5

Magnetorheology of dilute ferrofluids: Comparison of predictions of Brownian dynamics simulations and the ferrohydrodynamics equations

Denisse Soto-Aquino and Carlos Rinaldi

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Ferrofluids are colloidal suspensions of magnetic particles that exhibit normal liquid behavior in the absence of magnetic fields, but respond to imposed magnetic fields by changing their viscosity, the so-called magnetoviscous effect, without loss of fluidity. Although the magnetorheological response of ferrofluids is important for many established and emerging applications, its complete description is still lacking. Most prior efforts have been devoted to understanding the steady state magnetoviscous effect as a function of applied magnetic and shear fields and the related problems of transient and oscillatory response are largely unexplored. On the other hand, there are various competing continuum scale descriptions of the behavior of dilute ferrofluids, which require comparative studies to elucidate their relative advantages and limitations in describing ferrofluid flows. We have used rotational Brownian dynamics simulations to study the magnetoviscous response of dilute suspensions of spherical magnetic nanoparticles subjected to constant, transient, and oscillatory shear and constant magnetic fields. Results were compared with the predictions of the various ferrohydrodynamic governing equations, solved analytically or using numerical schemes. This presentation will provide a summary of these studies.

Tuesday Afternoon

Symposium SG

Rheology of Solids, Glasses and Composites

Organizers: Daniel J. Lacks and Sadhan C. Jana

Tuesday 1:30 Amphitheater A SG6

Durometry of yield stress materials

Adam W. Mix and A. Jeffrey Giacomin
Rheology Research Center, University of Wisconsin, Madison, WI 53706, United States

A material that can withstand a finite amount of stress before it flows is said to have a yield stress. Any stress falling below the yield stress of the material does not cause flow. No flow does not mean no deformation though. Deformation below the yield stress is elastic, and this is usually ignored. For some pastes, we can characterize this elastic deformation below the yield stress with a Young's modulus. We use a durometer to measure this modulus, employing a standardized, spring loaded indentor. When the durometry leaves no mark on the tested surface, we know that the indentation is governed by linear elastic indentation mechanics, and we can then relate the standardized hardness scale reading (TYPE OO ASTM D2240) to the Young's modulus of the yield stress material.

Tuesday 1:55 Amphitheater A SG7

Nonlinear mechanics of glassy polymers

Greg D. Zartman, Xin Li, and Shi-Qing Wang
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We carry out mechanical tests to examine the consensus that higher entanglement density (polycarbonate vs polystyrene) favors yielding. One challenge to this idea is the widely known fact that properly aged PC could also show brittle failure behavior. Thus, there are clearly some other factors important to account for the different failure behaviors. That pre-deformed PS becomes ductile and shows yielding and necking is another phenomenon that may not be fully consistent with the simple correlation between entanglement density and structural failure of polymer glasses. In this work, we carry out systematic Instron type stress strain curve measurements of different glassy polymers including PC, PS and PMMA that are either prepared in quiescence or pre-deformed. We will report various failure behaviors observed under different external conditions to elucidate the relationship between mechanics and molecular structure in polymer glasses.

Tuesday 2:20 Amphitheater A SG8

Physical aging of an epoxy film subjected to carbon dioxide plasticization jumps: Evidence of a new glassy state

Shankar Subramanian[1], Gregory B. McKenna[2], and Jing Zhao[2]
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Structural recovery and physical aging of glassy polymers after temperature jumps have been very well studied in the literature [1, 2]. On the contrary, there is only limited work available on the aging and recovery behaviors of glassy polymers subjected to plasticizer jumps. We have shown in our previous works, using moisture and carbon dioxide as the plasticizing environments, that qualitatively they mimic the behaviors of temperature jumps but quantitatively they are different [3, 4, 5, 6]. Further, the structural recovery results for temperature and carbon dioxide plasticizer jump experiments to the same final condition showed evidence of a new glassy state [6]. In the present work, we further investigate this anomalous behavior by studying the physical aging behavior of an epoxy film subjected to carbon dioxide pressure jumps and compare the results with temperature jump experiments such that the final conditions of these experiments are same. The results concur with the behavior seen in the structural recovery experiments and we observe evidence for the existence of a new glassy state.

References: [1] Kovacs, A.J., Fortschritte der. Hochpolymeren-Forschung, 3, 394-507, 1963. [2] Simon, S.L., Sobieski, J.W., and Plazek D.J., Polymer, 42, 2555-2567, 2001. [3] Zheng. Y., and McKenna, G.B., Macromolecules, 36, 2387-2396, 2003. [4] Zheng. Y., Priestley R.D., and McKenna, G.B., J. Polym. Sci., Part B: Polym. Phys., 42, 2107, 2004. [5] Alcoutlabi, M., Briatico-Vengosa, F., and McKenna, G.B., J. Polym. Sci., Part B: Polym. Phys., 40, 2050-2064, 2002. [6] Alcoutlabi, M., Banda, L., Kollengodu Subramanian, S., Zhao, J., McKenna, G.B., Macromolecules, DOI: 10.1021/ma1027577.

Tuesday 2:45 Amphitheater A SG9

Segmental dynamics in polystyrene melts

Hiroshi Watanabe[1], Yumi Matsumiya[1], and Tadashi Inoue[2]
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Atactic polystyrene (PS) has the type-B dipole perpendicular to the chain backbone so that its segmental motion activates the dielectric relaxation. For oligostyrene (OS) and PS samples of various molecular weights M, details of this motion were examined at temperatures T well above Tg through comparison of the complex modulus, G* = G' + iG", and the complex dielectric permittivity, e* = e' - ie". For OS, G*(w) and e*(w) fully relaxed through the segmental dynamics thereby exhibiting respective terminal relaxation tails, G'(w) ~ w^2, G"(w) ~ w, De'(w) = e'(0)-e'(w) ~ w^2, e"(w) ~ w, at low angular frequencies w below the segmental relaxation frequency. For PS, G*(w) relaxed partly through the segmental dynamics and then exhibited the polymeric full relaxation characterized by the Rouse-like behavior followed by the terminal flow behavior (with/without intermediate entanglement plateau depending on M). In contrast, e*(w) of PS still relaxed completely through the segmental dynamics. A ratio of the dielectrically and viscoelastically detected segmental relaxation times, r(M), and the dielectric intensity, De(M), decreased with increasing M up to M* = 2000 and then became insensitive to M on a further increase of M. The viscoelastic segmental relaxation reflects the cooperative torsion of the repeating units along the molecular backbone, while the dielectric segmental relaxation detects reorientational motion of those units affected by both intra- and intermolecular cooperativity. The observed decreases of r(M) and De(M) suggested that the dimension Lm of the whole OS molecule is smaller than the length scale Lc for the intermolecular cooperative motion and that Lm approaches Lc on an increase of M up to M*. Consequently, high-M PS having Lm > Lc exhibited the M-insensitive r(M) and De(M). Thus, the crossover molecular weight M* = 2000 can be taken as the molecular weight of the cooperative sequence along the PS backbone.

Tuesday 3:35 Amphitheater A SG10

Shape memory behavior of POSS-based thermoplastic polyurethanes

Xinzhu Gu and Patrick T. Mather
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Shape memory polymers (SMPs) have been proposed for biomedical applications due to their ability to recover to a predetermined shape in vivo and to realize highly controlled deployment. Devices from SMPs can be preprogrammed to recover at body temperature, resulting in natural deployment, thus eliminating the need for auxiliary heating devices. When inserted into the obstruction of blood vessels, gastrointestinal tract, or the bile duct, the SM scaffold is usually under stress, which may decrease its recovery ratio. The goal of this research is to develop thermoplastic SMPs with good shape recovery with optimal recovery sharpness and recovery stress pertinent to medical applications. POSS-based thermoplastic polyester-urethanes (POSS-TPU) are selected as the candidates given their good shape memory ability and tunable glass transition temperatures (T_g) based on our earlier study. Thus, a hybrid TPU system that incorporates a poly (D,L-lactide)/polycaprolactone soft block with a hard block containing the polyhedral oligosilsesquioxane (POSS) moiety was synthesized with T_g around body temperature. The free recovery and the constrained recovery responses of the polymer films were extensively studied as a function of the prior "fixing" deformation temperature (T_d). The sharpness of the free recovery transition was found to depend strongly on T_d. When deforming right at T_g of the materials, the sharpest recovery transition was achieved. Interestingly, in the constraint recovery study, it was found that when deforming at T_g, the fully-constrained stress (FCS), under which the materials are supposed to exhibit no recovery, exhibited the highest value. We conclude that this polymer system offers the sharpest recovery and highest FCS when the deformed at T_g, which can be controlled to be precisely body temperature.

Tuesday 4:00 Amphitheater A SG11

Rheology and structure of soft colloids

Praveen Agarwal, Samanvaya Srivastava, and Lynden A. Archer
Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Soft colloids have attracted significant interest recently as model systems for studying the glass transition and glassy fluids rheology, originating in part from their less fragile behavior as compared to hard sphere colloids. We recently reported on a new class of soft colloids created by densely grafting oligomers to nanoparticles. Termed Nanoscale ionic materials (NIMs), these systems display fluid like properties in absence of any solvent, and consequently allow glassy fluid physics and rheology to be studied without complications from enthalpic interactions between the solvent and suspended phase. This talk focuses on the effect of "softness" on the structure and dynamics of soft glasses. Specifically, by varying the molecular weight and grafting density of the tethered polymer chains, we are able to design self-suspended, jammed materials with varying elastic modulus and yield stress that manifest strong dependence on the softness. Surprisingly, we also find that temperature plays a significant role on the glassy dynamics of NIMs - with higher temperatures leading to increased solid-like rheological response. Mechanical rheology, small angle X-ray scattering and broadband dielectric spectroscopy are used to study this behavior experimentally. Experimental analyses are supported with theoretical studies within the Soft Glassy Rheology (SGR) framework.

Tuesday 4:25 Amphitheater A SG12

Diffusion of polymer-grafted nanoparticles in polymer melts

David L. Green and Maura E. McEwan
Chemical Engineering, University of Virginia, Charlottesville, VA 22903, United States

We probed the dynamics of uniform dispersions of polymer-grafted nanoparticles in polymer melts with x-ray photon correlation spectroscopy (XPCS). Analysis of the characteristic relaxation times revealed Brownian diffusion below the entanglement molecular weight of the melt polymer, and inhibited dynamics above the entanglement molecular weight. The self-diffusivity of the nanoparticles, i.e., diffusivity of the nanoparticles relative to that at infinite dilution was slower in the lower molecular weight melt due to the greater stretching of the graft polymer. In accord with theory, nanoparticle self-diffusivities in melts of varying molecular weights scale with respect to the effective volume fraction when considering the particle core and polymer brush as a hard sphere. Further, we show a correspondence between the scaled nanoparticle diffusivity and the low-shear viscosity - the first time this has been carried out in polymer melts.

Tuesday 4:50 Amphitheater A SG13

A simulation study on the effects of shear flow and nanotube shape on the electrical conductivity of carbon nanotube/polymer composites

Ali E. Eken[1], Emilio J. Tozzi[2], Daniel J. Klingenberg[3], and Wolfgang Bauhofer[1]
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We use particle-level simulations to simulate carbon nanotube (CNT)/polymer composites in simple shear flow. Electrical conductivities are measured using a resistor network algorithm. Effects of nanotube shape, tunneling effect and flow fields on the electrical conductivities of the composites are studied. Simulations showed that imposed shear flow can decrease the electrical percolation threshold. Helical nanotubes are more efficient than straight nanotubes in facilitating the formation of electrically connected agglomerates. We show that the rate of imposed shear flow influences the electrical conductivity of the composites. Increasing shear rate aligns the nanotubes in the flow-gradient direction and breaks down the connected agglomerates decreasing the composite conductivity. Anisotropy factor and orientation angle measurements are used to quantify the alignment of the nanotubes.

Tuesday 5:15 Amphitheater A SG14

Effect of mechanical percolation on the properties of nanocomposites

Marcio R. Loos and Ica Manas-Zloczower
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The mechanical percolation effect of two different fillers, namely carbon nanotubes (CNTs) and cellulose nanowhiskers on the elastic modulus of polymer based composites is investigated. We show that the critical filler volume fraction where a percolating network is forming marks a 'turning point' in the reinforcement efficiency. For composites containing cellulose whiskers a strong percolated network of species linked by hydrogen bonds is formed and the percolation threshold marks a positive 'turning point' in the reinforcement efficiency. In this case, at concentrations higher than the percolation threshold, the modulus of the composite increases dramatically. By contrast, in CNT based composites a percolated network not linked by hydrogen bonds is formed and the percolation threshold marks a negative 'turning point' in the mechanical performance. At volume fractions above the percolation threshold a decrease in reinforcement efficiency or even a detrimental effect can be observed. Different micromechanical models for the prediction of mechanical properties of nanocomposites, taking into consideration the degree of interaction between fillers are presented.

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Tuesday 1:30 Amphitheater B SC20

A theoretical study of active microrheology in concentrated colloidal suspensions

Ehssan Nazockdast and Jeffrey Morris
Chemical Engineering, Benjamin Levich Institute, CUNY, New York, NY 10031, United States

A theory based on the Smoluchowski equation is developed to predict the microstructure of hard sphere colloidal suspensions in active microrheology setup e.g. when a probe particle is pulled through a bath of colloidal particles with a constant external force F^{ext}. The theory is based on the observation that particles near contact are the controlling configuration in concentrated sheared suspensions, allowing use of pair-wise additive interactions and therefore explicitly accounting for many-body interactions. The probability distribution of bath particles with respect to the probe, $g(r)$, is determined from an integro-differential equation solved by iterative numerical methods at different set of Pe (ratio of external to Brownian forces) and solid volume fractions. The distribution is then used to compute the probe average mobility and the apparent shear viscosity. The macrorheology predictions of structure and rheology in simple shear flows based on a similar theoretical framework is provided to enable a comparison of the methods. The predictions of both cases are compared with the available simulations and experimental results.

Tuesday 1:55 Amphitheater B SC21

Decoupling of rotational and translational diffusion near the colloidal glass transition

Eric R. Weeks

Physics Dept., Emory University, Atlanta, GA 30030, United States

In regular liquids, particles and molecules undergo Brownian motion, causing them to both translate and rotate. For a given particle (or molecule) size and shape, the rates of these motions have a constant ratio. However, in supercooled molecular liquids close to the glass transition, this is not the case. The diffusion constants decouple: diffusion is very slow, but molecules translate faster than they rotate. We use a laser-scanning confocal microscope to simultaneously observe the rotational and translational dynamics of tetrahedral particle clusters in a dense colloidal “supercooled fluid”. We observe decoupling of rotational and translational diffusion in samples close to the glass transition volume fraction. This then suggests that supercooled liquids are not merely simple liquids with large viscosities, but that diffusion takes place by fundamentally changed mechanisms.

Tuesday 2:20 Amphitheater B SC22

Rheological behavior of binary mixtures of highly concentrated emulsions

Reza Foudazi, Irina Masalova, and Alexander Y. Malkin

Material Science and Technology, Cape Peninsula University of Technology, Cape Town, South Africa

The droplet size dependency of rheological behavior for highly concentrated emulsions (HCE) are generally monotonous regardless whether the size distribution is wide or narrow particularly when Sauter mean droplet size is considered. However, we have found that the dependence of the rheology on the relative content of components in binary mixtures of HCE with 0.85 volume fraction demonstrates rather unusual behavior. The shear viscosity, yield stress and storage modulus plateau of investigated binary mixtures of different droplet size ratios showed a negative deviation from the mixing rule. This effect was more pronounced when droplet size ratio exceeded 6 where droplet size distributions of two components were overlapped only about 5%. The yield stress and plateau of storage modulus of this binary mixture with 20% of small droplet size was practically absent in contrast to the viscoplastic behavior of initial fractions. The solid-like behavior of highly concentrated emulsions is usually attributed to the formation of compressed droplets in emulsions, which is absent in the binary mixtures with droplet size ratio of more than 6 due to a possibility of efficient spatial filling with spherical droplets of different size.

Tuesday 2:45 Amphitheater B SC23

Dye absorption induced gelation of dilute suspensions of spherical and rod-like zinc oxide nanoparticles – a new route to gelation

Florian J. Stadler[1], Cyril Martini[2], Frédéric Fages[3], and Christian Bailly[4]

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The adsorption of the amphiphilic Ru^{II} complex Z907 onto the surface of ZnO nanospheres and nanorods causes the gelation of organic solvents, such as THF or acetone. The gels are thermally stable at very low concentration (nanoparticle volume fraction $\varphi = 0.009$), but mechanically fragile, the behavior being dependent on solvent nature, nanoparticle concentration, and Z907-to-ZnO molar:wt. ratio. Rheological experiments confirmed the solid component built up a network to give a viscoelastic gel-phase material with a rather low value of the storage modulus G' around 100 Pa, but all characteristics of a rubbery material. The brittleness of the manifests itself in a linear-viscoelastic limit around γ_0=0.1%.

However, TEM and SEM experiments did not give evidence that nanoparticle long-range ordering occurred under the experimental conditions investigated. Moreover, time-dependent SAXS measurements pointed to a decrease of the nanoparticles aggregates size upon gelation. All together, the data obtained might be rationalized in terms of aggregate-to-aggregate transition in solution, the primitive large aggregates giving rise to smaller ones upon reaction with Z907. The resulting smaller hybrid aggregates could be the active species that act as self-assembling components in the gelation process.

Given the interesting electronic and photonic properties of zinc oxide nanoparticles, such hybrid organic-inorganic gels could open new directions in materials sciences, low-cost electronics, and photovoltaics.

Reference: C. Martini, F. J. Stadler, A. Saïd, V. Heresanu, D. Ferry, C. Bailly, J. Ackermann, F. Fages, Langmuir 2009, 2009, 25, 15, 8473-79, DOI: 10.1021/la804280m.

Tuesday 3:35 Amphitheater B SC24

Yielding in dilute colloidal gels under transient flow

Hubert K. Chan, Bharath Rajaram, and Ali Mohraz

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Colloidal gels are encountered in a wide range of applications from ceramics and food processing to feedstocks in emerging technologies such as direct-write assembly. These materials are often subject to nonlinear deformations during their production and processing. Insights into the coupling between the macroscopic shear stresses and the thermodynamic and hydrodynamic interparticle interactions can lead to products with improved end-use properties. In this study, the evolution of dilute, depletion-induced colloidal gels under transient flow is investigated using quantitative confocal microscopy and rheology. A two-step yielding process is encountered with the secondary yielding event occurring at large values of accumulated strain. The microstructural signatures of the transition to this nonlinear mode of gel yielding are visualized and quantified in real space. Shearing the gel beyond the secondary yield point results in a terminal microstructure characterized by dense clusters and large voids, reminiscent of phase-separating mixtures. We discuss the implications of this phenomenon on the phase behavior and rheology of colloidal gels.

Tuesday 4:00 Amphitheater B SC25

Induced failure in colloidal gel stabilized particles suspensions

Marco Caggioni, Seth E. Lindberg, and Patrick T. Spicer

Complex fluids microstructures, Procter & Gamble, West Chester, OH 45069, United States

Colloidal gel has been reported to exhibit different instabilities such as compression and collapse [1,2]. These instabilities are caused by the gravitational stress acting on the gel proportionally to the density difference between the gel's colloids and the liquid in which they aggregate.

We find that gel compression and collapse can also be observed in density matched system when secondary particles are trapped in the colloidal gel. The additional stress provided by the suspended particles propagates through the gel structure producing instabilities that can be interpreted by considering the weighted average density of the gel's colloids and the trapped particles.

[1] "Gravitational compression of colloidal gels" J.J. Liétor-Santos , C. Kim, P.J. Lu, A. Fernández-Nieves, and D.A. Weitz, Eur. Phys. J. E 28, 159 (2009). [2] "Gravitational Collapse of Colloidal Gels" S. Manley, J. M. Skotheim, L. Mahadevan, and D. A. Weitz, Physical Review Letters 94, 218302 (2005)

Tuesday 4:25 Amphitheater B SC26

Rheology and microstructure of a colloidal gel undergoing high strain-rate yielding

Lilian C. Hsiao and Michael J. Solomon

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The mechanism of yielding in colloidal gels, particularly for high strain-rate deformations that are typical of practical applications, is not fully understood. Here, we examine the oscillatory response and stress relaxation of a colloidal gel formed by short-range depletion interactions to find a correlation between the macroscopic rheological behavior and their microstructural features. We use confocal laser scanning microscopy to directly visualize the evolution of 3D structure of the colloidal gel. The colloids are monodisperse, micron-sized poly(methyl methacrylate) spheres ($\varphi = 0.2$, $c/c^* = 0.55$, $\xi = R_g/R = 0.08$, $U_{contact}/k_BT \sim 10$) dispersed in a refractive index and density matched solvent. We impose simple shear flows of various strains on the gel and observe the 3D structural change after deformation. We accomplish this by using a UV light-triggered photopolymer, which allows particle configurations to be locked in place rapidly (<0.6s) after yielding. We characterize the transition from a dense network to free clusters of particles as a function of the applied strain, and we quantify this local and global structural change using the measures of contact number distribution, cluster size distribution, and number density fluctuations.

Tuesday 4:50 Amphitheater B SC27

Thermosensitive nanoemulsion “organohydrogels” with surprisingly solid-like rheology

Matthew E. Helgeson, Shannon E. Moran, and Patrick S. Doyle

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We report the discovery of a novel class of "organohydrogels" based on oil-in-water nanoemulsions where the aqueous phase contains functionalized polyethylene glycols (PEGs). For emulsions with average drop sizes below ~100 nm, dispersions exhibit a thermoreversible transition from a low-viscosity liquid to a viscoelastic solid with remarkably high moduli for a liquid-liquid dispersion. Combined rheology and neutron scattering measurements reveal striking similarity of the organohydrogels to hard particle colloidal gels, including fractal-like microstructure and modulus scaling. The gelation occurs over a wide range of conditions (volume fraction, PEG concentration, droplet size), and the gel temperature and ultimate modulus are highly sensitive to the PEG functional chemistry. Thus, we hypothesize that gelation results from thermally-induced self-assembly of functionalized PEGs at the oil-water interface, leading to bridging-mediated attractions between droplets. The utility of the material system is illustrated by the use of crosslinkable PEGs, enabling the suspension microstructure to be "frozen" through photopolymerization, yielding soft nanocomposites with highly tunable mechanical and transport properties.

Tuesday 5:15 Amphitheater B SC28

Gelling and ungelling blood

Matthew B. Dowling[1] and Srinivasa Raghavan[2]
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When a wound occurs, the body initiates the clotting cascade whereby a clot is formed at the wound site. The clot is a gel of the protein fibrin, and the blood cells are immobilized within this gel. Gelation of blood is thus critical to prevention of blood loss from serious wounds, e.g., in the case of accident victims or soldiers on the battlefield. At the same time, if a gel (clot) travels through the body, it could lead to stroke - therefore, it is desirable to be able to reverse such gelation. Here, we show the ability to both gel blood using a biopolymer and reverse the gelling using a sugar-based supramolecule. The biopolymer is a hydrophobically modified (hm) derivative of the polysaccharide, chitosan. When hm-chitosan is contacted with heparinized human blood, it rapidly transforms the liquid into an elastic gel. In contrast, the native chitosan (without hydrophobes) does not gel blood. Gelation occurs because the hydrophobes on hm chitosan insert into the membranes of blood cells and thereby connect the cells into a sample-spanning network. The above process can be readily reversed by the addition of a-cyclodextrin, a supramolecule having an inner hydrophobic pocket. When the cyclodextrin is added, polymer hydrophobes detach from blood cells and embed within the hydrophobic pocket of the cyclodextrin, thereby disrupting the cell network. We are currently testing hm-chitosan bandages as low-cost hemostatic dressings for use by trauma centers and the military. Preliminary tests with small and large animal injury models show its efficacy at achieving rapid hemostasis. [Reference: Dowling et al., Biomaterials, 32, 3351 (2011).]

Symposium FS

Non-Newtonian Flows and Stability

Organizers: Rob Poole and Fernando T. de Pinho

Tuesday 1:30 Founders Ballroom A FS1

The Rayleigh plateau instability on a highly stretched viscoelastic filament

Christian Wagner
Physics, Saarland University, Saarbreucken, Germany

When a dilute polymer solution experiences capillary thinning, the finite time singularity of the pinch off process is suppressed and an almost uniformly cylindrical thread is formed. The flow within the thread is supposed to be purely elongational and the experiment can be used to extract some information on the elongational viscosity of the solutions. However, there is a debate how finally the thread will break and different models that predict a Newtoninan like self-similar behavior have been presented. In our experimental studies we find that in the last stages of thinning, when polymers have become fully stretched, the filament becomes prone to a Rayleigh-Plateau instability. This is the case for the whole variety of different either isolated or coherently growing droplets that ultimately form the well known beads-on-a-string-pattern. For sufficiently high polymer concentrations, the filament eventually separates out into a ``solid'' phase of entangled polymers, connected by fluid beads. A solid polymer fiber of about 100 nanometer thickness remains, which is essentially permanent.

Tuesday 1:55 Founders Ballroom A FS2

The viscoelastic bungee jumper: Constant force extensional rheometry of polymer solutions

Christian Clasen[1], Gareth H. McKinley[2], and Peter Szabo[3]
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We revisit the rapid stretching of a liquid filament under the action of a constant imposed tensile force, a problem which was first considered by Matta & Tytus [JNNFM vol. 35, pp 215-229, 1990]. A liquid bridge formed from a dilute polymer solution is first established between two cylindrical disks. The upper disk is held fixed and may be connected to a force transducer while the lower cylinder falls due to gravity. By varying the mass of the falling cylinder and measuring its resulting acceleration as well as the filament profile, the viscoelastic nature of the elongating fluid filament can be probed. In particular, we show that it is possible to readily impose very large material strains and strain rates so that the maximum extensibility of the polymer molecules can be quantified. This unique characteristic of the experiment is analyzed numerically using the FENE-P model and two alternative kinematic descriptions; employing either an axially-uniform filament approximation or a quasi two-dimensional Lagrangian description of the elongating thread. Based on these theoretical considerations we develop an expression that enables estimation of the finite extensibility parameter characterizing the polymer solution in terms of quantities that can be extracted directly from simple measurement of the time-dependent filament diameter.

Tuesday 2:20 Founders Ballroom A FS3

Stability of fiber spinning under filament pull-out conditions

Carina van der Walt[1], Martien A. Hulsen[1], and Arjen C. Bogaerds[2]

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In fiber spinning, a polymeric fluid is pushed through a spinneret and drawn at high winding velocities to form filaments. Flow instabilities of filaments in the form of draw resonance can result in radius fluctuations which impose limitations on the production rate. Additionally, the filaments in fiber spinning can be pulled out of the die at high winding velocities if the fluid strength is sufficiently high [Bulters et al., J. Non-Newton. Fluid, 38:43-80, 1990]. The force balance between the integrated normal stress that occurs during flow in the upstream region and the spinning force determines the detachment point of the filament from the spinneret wall. Filament pull-out complicates the stability analysis in the sense that the upstream boundary conditions now depend on the position in the spinneret. In addition, the filament length varies in time. In this work we extend the stability analysis on fiber spinning of a single isothermal filament by including the upstream pull-out condition in a one-dimensional fiber spin model using the eXtended Pom-Pom (XPP) constitutive model of Verbeeten et al. [J. Rheol., 45(4):823-843, 2001]. Using spectral methods, our analysis incorporates the detachment point which is allowed to vary according to the prescribed (negative) slope S of the upstream integrated normal stress. Changing the slope S for a certain DR (draw ratio) and De (Deborah) number, the growth rate for each S value can be determined. We compare the stability regions of our fiber spin model with and without pull-out for different S values. For low De values a finite value of S is destabilizing the flow whereas for higher De values there is a range of S values that stabilizes the flow. For S = 0 we obtain fiber spinning with a constant force at pull-out, but the critical DR is greatly reduced. This is in contrast to fixed length fiber spinning of a Newtonian fluid at a constant force which is known to be stabile for any DR [Renardy, SIAM J. Appl. Math., 66:1261-1269, 2006].

Tuesday 2:45 Founders Ballroom A FS4

Studying origins of different failure modes in uniaxial extension of entangled polymer melts

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Entangled polymer melts tend to undergo failures during startup uniaxial extension or after step extension [J. Rheol. 52, 1275 (2008)]. Depending on the applied Hencky rates, different types of breakup or non-uniform extensions occur, including rupture analogous in appearance to the fracture of a cross-linked rubber. We will apply our insights gained from the PTV (Particle Tracking Velocimetry) studies of shear deformation behavior to learn about the origins of these various failure modes, either during startup extension or after step extension. In particular, we will characterize the kinematics of the deformation and identify the conditions for each type of specimen breakup.

Tuesday 3:35 Founders Ballroom A FS5

Linear instabilities in channel flows with constrictions: Two distinct elastic instabilities

Tim Reis[1], Mehmet Sahin[2], and Helen J. Wilson[3]

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We investigate the stability of a polymer melt flowing through a channel with constrictions. We model the fluid using the Rolie-Poly constitutive equation with a small additional solvent viscosity. We compute a 2D steady state numerically, using the technique introduced in [1], and calculate its linear stability to 3D perturbations as in [2]. The Reynolds number is zero throughout, so any instabilities we find are purely elastic.

In a geometry with a strong constriction, the 8:1:8 contraction-expansion flow, we find a purely two-dimensional instability [3], which compares well with experiments carried out on monodisperse linear polystyrenes in the Cambridge Multi-Pass Rheometer. In a less extreme geometry, the dominant instability is three-dimensional and its mechanism is thought to be the curved-streamline mechanism of [4]. The critical difference between the two geometries seems to be the amount of chain stretch in the base flow.

[1] M Sahin, H J Wilson. A semi-staggered dilation-free finite volume method for the numerical solution of viscoelastic fluid flows on all-hexahedral elements. Journal of Non-Newtonian Fluid Mechanics, vol. 147, pp. 79-91, 2007. [2] M Sahin, H J Wilson. A parallel adaptive unstructured finite volume method for linear stability (normal mode) analysis of viscoelastic fluid flows. Journal of Non-Newtonian Fluid Mechanics, vol. 155, pp. 1-14, 2008. [3] D G Hassell, M R Mackley, M Sahin, H J Wilson, O G Harlen, T C B McLeish. Molecular physics of a polymer engineering instability: experiments and computation. Physical Review E, 77(5), pp. 050801, 2008. [4] P Pakdel, G H McKinley. Elastic instability and curved streamlines. Physical Review Letters 77, pp. 2459-2462, 1996.

Tuesday 4:00 Founders Ballroom A FS6

Purely elastic instabilities in serpentine channels

Anke Lindner[1], Josephine Zilz[1], Rob J. Poole[2], and Manuel A. Alves[3]
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Purely elastic instabilities are known to occur in flows with curved streamlines of viscoelastic fluids at low Reynolds numbers (Re). They have recently attracted renewed interest as they have been shown to increase mixing in wavy microchannels [1]. The onset of instability has been proposed to be a function of the balance between streamline curvature and hoop normal stresses [2], but the exact form of this relation is scarcely studied, in particularly for channel flow. Here we report the results of a combined experimental and numerical investigation of variation of the instability threshold with the channel curvature.

The experimental study is performed for a dilute polymer solution in a wavy microchannel. The channel of width W comprises a series of half loops of radius R which is systematically varied. We have analyzed the critical Weissenberg number (Wi_c) at which the flow becomes unstable as a function of the geometry of the channel and the properties of the polymer solution.

The numerical simulations study the creeping flow limit (Re = 0) for a viscoelastic fluid obeying the upper-convected Maxwell model. Two-dimensional simulations matching the experimental conditions show that above a critical Weissenberg number the flow becomes unsteady. Good qualitative agreement between experiments and simulations is obtained and we show that the instability onset Wi_c is proportional to the square root of R/W with a small offset when R/W tends towards zero. These results are confirmed by a simple scaling argument following the Pakdel-Mckinley criterion [2].

[1] A. Groisman and V. Steinberg, New J. Phys. 6, 29 (2004). [2] P. Pakdel and G. H. McKinley. Physical Review Letters, 77(12):2459-2462, 1996.

Tuesday 4:25 Founders Ballroom A FS7

Numerical simulation of electro-elastic instabilities

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Even though electro-osmotic flows (EOF) of complex fluids at microscale are still in a state of exploratory research, there are practical applications where its advantages stand out clearly, such as in screening for protein crystallization, bio-analyses or the manipulation of multiphase flows. Here, electrokinetic forcing, through such mechanisms as electro-osmosis or electrophoresis, are obvious candidates to accurately control the flow in microfluidic devices. This electrokinetic forcing can lead to the onset of flow instabilities, called electrokinetic instabilities, even when Newtonian fluids are used [1,2]. However, when electrokinetic forcing is used in combination with viscoelastic fluids, new phenomena arise, as recently discovered by Bryce and Freeman [3] and the mechanisms driving these electro-elastic instabilities need to be thoroughly investigated.

In this work we perform numerical EOF simulations of viscoelastic fluids in complex geometries, with the ultimate goal of studying and understanding the mechanism behind the onset of electro-elastic instabilities. We use a finite volume method to solve the relevant coupled governing equations for electro-osmotic flows of viscoelastic fluids, namely the nonlinear Poisson- Nernst-Planck equations that govern the electrical double-layer field, the Cauchy equation with a body force due to the applied electrical potential field and a variety of constitutive equations for the viscoelastic fluids, in particular the upper-convected Maxwell and simplified Phan-Thien-Tanner models. In addition to the simulations in complex geometries (cross-slot flow and flow past sharp corners), some predictions are compared with recent analytical solutions for the fully-developed flow in a two-dimensional microchannel.

References: [1] M.H. Oddy, J.G. Santiago and J.C. Mikkelsen, Anal. Chem., 73:5822-5832 (2001); [2] J-K. Chen and R-J. Yang, Microfluid Nanofluid, 5:719-725 (2008); [3] R. M. Bryce and M. R. Freeman, Lab Chip, 10:1436-1441 (2010).

Tuesday 4:50 Founders Ballroom A FS8

A Stokesian viscoelastic flow: Transition to oscillations and mixing

Becca Thomases[1], Michael Shelley[2], and Jean-Luc Thiffeault[3]
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To understand observations of low Reynolds number mixing and flow transitions in viscoelastic fluids, we study numerically the dynamics of the Oldroyd-B viscoelastic fluid model. The fluid is driven by a simple time-independent forcing that, in the absence of viscoelastic stresses, creates a cellular flow with extensional stagnation points. We find that at O(1) Weissenberg number these flows lose their slaving to the forcing geometry of the background force, become oscillatory with multiple frequencies, and show continual formation and destruction of small-scale vortices. This drives flow mixing, the details of which we closely examine. These new flow states are dominated by a single-quadrant vortex, which may be stationary or cycle persistently from cell to cell.

Tuesday 5:15 Founders Ballroom A FS9

On the critical conditions for purely-elastic instabilities

Rob J. Poole

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It is widely accepted that the flow of viscoelastic fluids can become unstable above a critical flow speed. Such instabilities can occur even in the absence of significant inertial effects (i.e. the Reynolds number tending to zero) where equivalent Newtonian fluid flows remain stable. These "purely-elastic" instabilities arise from the interaction of streamline curvature and strong elastic (normal) stresses. Based upon experimental evidence in a range of geometries, and some linear stability analysis results, McKinley et al. [1] proposed a dimensionless criterion for the onset of such elastically-driven instabilities. The present talk discusses the results of a series of finite-volume calculations of viscoelastic fluid flow in a range of geometries to investigate the critical value of this dimensionless criterion.

[1] McKinley et al. J. Non-Newt. Fluid Mech. 67:19-47 (1996)

Symposium MB

Rheology of Polymer Melts and Blends

Organizers: Joao Maia and Avraam I. Isayev

Tuesday 1:30 Founders Ballroom B MB15

Cocontinuous blends for producing porous membranes

Christopher W. Macosko, Aaron Hedegaard, and Milana Trifkovic

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Microporous films serve as battery separators and as support layers for gas separation membranes. Average pore size, pore size distribution, pore wall functionality and thickness of the support layer play a vital role in the overall performance of these films. Microporous membranes are created by extracting polyethylene oxide (PEO) from cocontinuous blends of PEO with polyethylene (PE). The PE/PEO blends using non-functional and maleic-anhydride functional PE (PE-g-MA) were mixed in a batch microcompounder and continuously in a pilot scale co-rotating twin-screw extruder. The effect of blend composition, shear rate, residence time, and annealing time on the cocontinuous morphology were investigated. The morphology and phase size of the blends was examined using SEM (scanning electron microscopy) and LSCM (laser scanning confocal microscopy). In order to satisfy the LSCM requirements of specimen transparency and fluorescence of one phase, hydroxyethyl(methacrylate) (HEMA) stained with rhodamine B dye was polymerized inside of the pores of the porous PE sheet. Rheological characterization of the blends with droplet and cocontinuous morphologies was performed. The rheology of droplet blends was fit to the Palierne viscoelastic droplet model to quantify the equilibrium interfacial tension of PE/PEO blends using both PE and PE-g-MA. Cocontinuous blend rheology was investigated over annealing time to predict coarsening behavior.

Tuesday 1:55 Founders Ballroom B MB16

Effects of phase-separation on the rheological, morphological and conductive properties of blends containing CNTs or graphene

Suryasarathi Bose[1], Ceren Ozdilek[1], Jan Vermant[1], Christopher W. Macosko[2], and Paula Moldenaers[1]

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The effects of the presence of multiwall carbon nanotubes (MWNTs) or thermally reduced graphene sheets (TRG) in a lower critical solution temperature blend (LCST blend) have been investigated by melt-rheology, conductivity spectroscopy and microscopic techniques. The phase separation has been characterized by melt-rheology as the system passes through the binodal and the spinodal lines of the phase diagram. Evolution of G' as a function of temperature and time was used as a probe to investigate the thermodynamics and kinetics of phase separation respectively. For example it was observed that the presence of TRG significantly influenced both the phase separation temperature and the shape of the phase diagram. The state of dispersion of the CNTs and FGS in the blends was assessed using rheology and conductivity spectroscopic measurements. Interestingly, the composite samples (mono-phasic) were virtually insulators at room temperature whereas highly conducting materials were obtained as a result of phase separation in the bi-phasic materials at elevated temperatures. By quenching these phase separated blends, the morphology was frozen and the conductivity could be retained in the solid state at room temperature. Electron microscopic images revealed that the phase separation resulted in a heterogeneous distribution of MWNTs or TRG in the blends, driven by thermodynamic forces, which led to an increase in their local concentration in a specific phase, potentially resulting in effective percolation.

Tuesday 2:20 Founders Ballroom B MB17

Effect of diblock copolymers on droplet coalescence, emulsification, and aggregation in immiscible homopolymer blends

David L. Green[1], Jeremy Fowler[2], Renlong Gao[3], Tomonori Saito[3], Eric Fried[4], and Timothy Long[3]

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Using rheo-optical techniques, we investigated the impact of interfacial wetting of symmetric diblock copolymers (BCPs) on the coalescence and aggregation of polydimethylsiloxane (PDMS) droplets in immiscible polyethylene-propylene (PEP) homopolymers. Anionic polymerization was used to synthesize well-defined matrix homopolymers and PDMS-b- PEP diblock copolymers with low polydispersity (PDI ˜ 1.02) as characterized with size exclusion chromatography and nuclear magnetic resonance spectroscopy. Blends were formulated to match the viscosities between the droplets and the matrix. Moreover, molecular weights of these components were varied to ensure that the inner block of the copolymer inside the droplet was collapsed and dry, whereas the outer block of the copolymer outside of the droplet was stretched and wet. Droplet breakup and coalescence as well as interfacial surface tensions were measured using rheo-optical experiments with Linkam shearing stage and an optical microscope. Subsequent to droplet breakup at high shear rates, we found that the BCPs mitigated shear-induced coalescence at lower shear rates. Increased BCP stretching was inferred from surface tension measurements, which indicate that BCP stretching causes the droplet surface to saturate at lower BCP coverages in line with theoretical predictions from wet-dry brush systems. Droplet aggregation was detected with further reductions in shear rate, which was attributed to the dewetting of the matrix from a saturated brush. Ultimately, the regions of droplet coalescence and aggregation were scaled by balancing the forces of shear with those due to the attraction between BCP-coated droplets.

Tuesday 2:45 Founders Ballroom B MB18

A study on influence of nanosilica in determining morphology of ternary blends: With emphasize on core-shell morphology

Zeinab Javidi and Hossein Nazockdast

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The core-shell morphology development in ternary blends is significantly controlled by thermodynamic parameters such as spreading coefficient. In the present work, an attempt was made to study the effect of nanosilica on interfacial interactions of the blend components, and on morphology development of HDPE/PS/PMMA(80/7/13 wt%) ternary blend. The nanocomposite blend samples with the mentioned blend ratio, but varying in nanosilica content (0,2,4 wt%), as well as the binary and ternary blend samples were prepared by melt blending. The melt linear viscoelastic results obtained from oscillatory tests exhibited a slight low frequency non-terminal storage modulus which could be related to a core-shell type morphology of the ternary system. This result was supported by a greater positive deviation of the ternary system's storage modulus from Palierne model in comparison with binary systems' at low frequency. The stress relaxation test also showed a higher residual stress as a consequence of a greater chain constraint in the ternary blend system. Further evidences were obtained from SEM micrographs which showed a core-shell type morphology. In addition, it was demonstrated that the nonosilica particles had an enhancing or a deteriorating effect on core-shell morphology depending on the affinity between the nanosilica particles and the blend components. Furthermore, the order of feeding and therefore the kinetic of mixing could also play a role.

Tuesday 3:35 Founders Ballroom B MB19

Entanglement relaxation in miscible polymer blends

Hiroshi Watanabe

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Viscoelastic, dielectric, and rheo-optical behavior was examined for miscible blends of high-M cis-polyisoprene (PI) and poly(p-tert-butylstyrene) (PtBS). The slow dielectric relaxation of the blends was exclusively attributed to the global motion of the PI chains having the type-A dipoles. The PI and PtBS chains behaved as the fast and slow (low- and high-friction) components and were well entangled with each other. The dynamics of these chains changed significantly with temperature T. At high T, the blend exhibited two-step entanglement plateau of the storage modulus G', and the plateaus at high and low angular frequencies (w) were attributed to the entanglement among all component chains and that between the PtBS chains, respectively. At low T, the blend exhibited the Rouse-like power-law behavior of storage and loss moduli, G'=G"~w^0.5, in the range of w where the high-w plateau was supposed to emerge. This lack of the high-w plateau was attributed to retardation of the Rouse equilibration of the PI chain over the entanglement length a due to the hindrance from the slow PtBS chains: The PI and PtBS chains appeared to be equilibrated cooperatively/simultaneously at a rate essentially determined by PtBS. The Rouse equilibration time, evaluated from the G* data of the blend, was just moderately shorter than the dielectrically determined relaxation time of PI. Thus, the high-w plateau zone was too narrow to be resolved experimentally, and the PI chains relaxed almost immediately after their Rouse equilibration (retarded by PtBS). This PI relaxation activated the constraint release (CR) relaxation of PtBS to dilate the entanglement mesh for PtBS. A simple model considering the Rouse equilibration and CR/dilation processes described the G* data of the blend surprisingly well. The model calculation was consistent with the rheo-optical data, lending support to the molecular picture underlying the model.

Tuesday 4:00 Founders Ballroom B MB20

A visco-hyperelastic formulation for the rheology of immiscible blends

Donggang Yao
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It has recently been shown that the dynamics of complex interfaces can be treated by hyperelastic finite deformation, and the Cauchy stress tensor can be written as a tensor derivative of the interfacial energy. In the present study, the analytical nature of this tensor derivative was further explored, resulting in a more useful constitutive relation between the stress tensor and the Finger strain tensor. To accommodate the interfacial relaxation effects, an energy balance principle was adopted in developing a nonlinear relaxation model which was then used in a visco-hyperelastic formulation for stress determination. Case studies on this visco-hyperelastic model were performed, and validations against known results were attempted. While at small deformation rates, the new model agrees with the linear viscoelastic calculations, as well as Doi and Ohta's scaling predictions, high nonlinearity was observed at large deformation rates.

Tuesday 4:25 Founders Ballroom B MB21

Rheological behavior of DL-lactide-block-L-lactide copolymers and blends of poly(DL-lactide) and poly(L-lactide)

Norhayani Othman[1], Cuiling Xu[2], Parisa Mehrkhodavandi[2], and Savvas Hatzikiriakos[1]
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In this study, three different compositions of nearly monodispersed diblock copolymer of DL-lactide and L-lactide were synthesized by using ring-opening polymerization methods that utilize a chiral indium based catalyst for living enantioselective polymerization of lactide. The effects of molecular weight and block length ratio on the rheological behavior of DL and L- lactide diblock copolymers in disordered state were investigated. For comparison, blends of PDLLA and PLLA homopolymers of equivalent molecular weights to those of diblock copolymers were prepared. Linear viscoelastic shear oscillatory was performed at various temperatures. It is found that time-temperature superposition principle is applicable to the block copolymers and blends in the disordered state. The disordered state was determined from logarithm plot of storage modulus, G' versus loss modulus, G", at which the moduli become independent of temperature. The terminal zone behavior at low frequency is reached with characteristic slope of 1 and 2 for G" and G' respectively. The molecular weight dependence of zero shear viscosities of homopolymers, blends and diblock copolymers was also determined. The crystallization behavior was investigated using differential scanning calorimetry (DSC). The DSC thermograms of blends exhibited a single glass transition at about 50-60 °C followed by melting point of PLLA at temperature of 177 °C. With deceasing content of PLLA in the blends, the intensity of melting peak decreased. On the other hand, only block copolymer with longest (about 67 wt%) L-lactide block shows melting point after non-isothermal cooling at cooling rate of 5 °C/min.

Tuesday 4:50 Founders Ballroom B MB22

Rheological and morphological behavior of PP/PBT blends filled with multiwall carbon nanotubes

Ali Namadian Mojarrad and Hossein Nazockdast
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The main objective of this work was to study the effect of multiwall carbon nanotubes (MWNTs) on the morphology development of polypropylene/polybuthylene therephthalate /MWNT (PP/PBT/MWNTs) nanocomposites. All the samples varying in blend ratios (80/20, 50/50, and 20/80 wt% of PP and PBT) and MWNT content were prepared by means of melt compounding in an internal mixer. The ability of the blend components in dispersing of MWNTs evaluated in terms of melt linear and nonlinear viscoelastic results was found to be greater for PBT than PP. Linear viscoelastic results showed the localization of MWNT is controlled by thermodynamic parameters and mixing conditions (mixing time , feeding order) that could be supported by the results obtained from the samples prepared by using different order of feeding. Blends' morphology was characterized by scanning electron microscopy (SEM). The SEM results showed a decrease in PP dispersed phase due to the hindrance effect of MWNTs in the samples prepared by different orders of feeding, while in the case of the samples with PBT dispersed phase, this effect could only be observed in the samples prepared by direct feeding method. This was attributed to lower concentration of MWNTs in PP matrix compared to those samples in which PBT was matrix. Interestingly, the 50/50 PP/PBT blend without MWNT showed cocontinuous structure, however by adding 1 wt% MWNT it changed to sea island structure and again with increasing MWNT concentration, cocontinuous structure was observed.

Tuesday 5:15 Founders Ballroom B MB23

Linear and nonlinear viscoelastic behavior of particle containing immiscible polymer blends

Esmaeel Moghimi[1], Fatemeh Goharpey[1], and Reza Foudazi[2]
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In this study, rheological behavior of Polydimethylsiloxane (PDMS) / Polyisobutylene (PIB) model immiscible blend stabilized with micron - sized hydrophobic calcium carbonate particles with two different particle sizes was investigated. The recovery, step shear strain and frequency sweep experiments were carried out to probe the effect of particles on the flow induced coalescence. It was found that upon the addition of particles, flow induced coalescence was slowed down and with addition of 4 w% particles this phenomenon was almost suppressed. This effect became more obvious when the particle size was reduced. The presence of particles at the fluid-fluid interface was supported by wetting parameter calculation and verified by optical microscopy observations. Moreover, direct visualizations showed that the particles are able to form clusters of droplets by simultaneously adsorbing two fluid-fluid interfaces and glue dispersed droplets together. These particle-bridged droplet clusters lead to a plateau in storage modulus and an upturn in complex viscosity in the low frequency region during frequency sweep experiment. The deviation of blend system behavior from conventional Palierne's model towards Goharpey's model - which is a modification of Palierne's model by considering the aggregation of dispersed phase - suggested the application of aggregation models such as Coussot's model for this system. Furthermore, effect of particles on the nonlinear viscoelastic behavior of blend with stress growth response upon start-up of shear flow was investigated. The validity of Doi-Ohta scaling relationships (which is work out for particle free blends) in the presence of particles was evaluated.

Symposium MF

Microfluidics, Microrheology and Confined Systems

Organizers: Amy Shen and Pat Spicer

Tuesday 1:30 Room 204 MF20

Study of inertial effects in microrheology

Tsutomu Indei, Jay D. Schieber, Andres Cordoba, and Ekaterina Pilyugina
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The dynamic modulus G^* of a viscoelastic medium is often measured by following the trajectory of a small bead subject to Brownian motion in a method called passive microbead rheology. This equivalence between the positional autocorrelation function of the tracer bead and G^* was assumed via the generalized Stokes-Einstein relation (GSER). The GSER was first proposed by Mason and Meitz [Phys. Rev. Lett. *74*, 1250 (1995)], and its derivation was given by Mason five years later [Rheol. Acta *39*, 371 (2000)] on the basis of the apparently unstationary generalized-Langevin-equation (GLE) with the lower integral limit 0. However, inertia of both bead and medium is neglected in GSER so that the analysis based on GSER is not valid at high frequency where inertia is not negligible. We first derive the GSER that includes bead inertia on the basis of the explicitly stationary GLE with the lower integral limit $-\infty$. If bead inertia is considered, the mean-squared-displacement (MSD) oscillates well beyond the time scales of inertia, which is rather different from both the original result of GSER and what is typically observed for viscoelastic materials. What is more, the discrepancy from the GSER result becomes worse with decreasing bead mass. We resolve these paradoxes by a rigorous analysis of the system described by simple viscoelastic models. The modeling shows why oscillations have not been seen experimentally for the viscoelastic systems studied. We show that the presence of medium inertia and/or medium viscosity can attenuate the oscillations. Actually, such oscillations are possible for low-viscosity systems, as recently measured [Tongcang Li, et al., Science, *328*, 1673 (2010)]. Elimination of inertia is delicate.

Tuesday 1:55 Room 204 MF21

Multiple particle tracking (MPT) study on highly elastic fluids: Treatment of particle localization errors

Anne Kowalczyk and Norbert Willenbacher
Institute for Mechnical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Germany

Synthetic acrylic polymers are frequently used as thickening agents in water-based coatings, adhesives or personal care products. Typically, these commercial alkali-swellable acrylates form inhomogeneous partly aggregated or cross-linked solutions. Inter- and/or intramolecular aggregation is due to hydrophobic groups randomly distributed along the chains. Such thickener solutions cover a wide range of rheological behavior, ranging from weakly elastic almost Newtonian to highly elastic gel-like. Despite its high technical relevance, little is known about the contribution of the micro-scale inhomogeneities to the bulk viscoelastic properties. Here we use Multiple Particle Tracking (MPT) to quantify the degree of structural and mechanical microheterogeneity of such acrylic thickener solutions. MPT is more and more used to study local mechanical or rheological properties of soft matter on a 0.1-1 μm length scale. The basic idea is to monitor the Brownian motion of inert fluorescent tracer particles by means of digital video microscopy. Statistical analysis of tracer trajectories allows for a characterization of sample inhomogeneity and in the case of homogeneous fluids a generalized Stokes-Einstein equation relates their mean squared displacements to the bulk shear moduli. Various sources of error may lead to a misinterpretation. Static and dynamic errors, caused by noise and the finite exposure time of the imaging setup, can considerably alter the apparent dynamics of sample. Moreover, trajectory artefacts caused by unavoidable ambiguities due to indistinguishable tracer particles entering or leaving the focal plane can lead to misjudgement of fluid properties. The limitations of MPT measurements due to these inaccuracies in particle localization will be discussed and for different thickener solutions it will be demonstrated how to get accurate results for the bulk viscoelastic properties of homogeneous materials and a reliable characterization of local rheological properties in the case of inhomogeneous fluids.

Tuesday 2:20 Room 204 MF22

Simulations and analysis of passive microrheology data

Andres Cordoba, Tsutomu Indei, and Jay D. Schieber

Department of Chemical and Biological Engineering, Illinois Institute of Technology, chicago, IL 60616, United States

Viscoelastic properties of condensed soft matter can be estimated by following the trajectory of an embedded micron-sized particle in a method called passive microbead rheology. Data analysis of passive microbead rheology is usually based on formulas that relate bead displacement statistics to the dynamic modulus of the material in frequency-domain. Therefore methods of analysis require conversion of the data to the frequency-domain using FFT routines. These methods are known to introduce errors associated with frequency discretization and finite window size. Time-domain data analysis methods based on a single bead trajectory have been proposed as an alternative to the frequency-space formulas [J. Fricks et al., SIAM J. Appl. MATH. 69, 1277-1308 (2009)]. In that work, the time-domain data analysis algorithm was evaluated using synthetic bead paths generated using a generalized Langevin equation (GLE). We have expanded these ideas with the aim of performing Monte-Carlo simulations on synthetic data to evaluate and compare analysis algorithms. We have used Brownian dynamics simulations to generate long trajectories of beads embedded in viscoelastic materials. We use photon correlation spectroscopy algorithms to calculate the mean-squared displacement in real-time during the simulations. Our technique allows us to consider particles trapped in harmonic and an-harmonic potentials. Additionally, we show a straightforward way of eliminating momentum directly from the GLE to find an inertia-less GLE. Using this procedure the computational cost of the simulations can be reduced by nearly five orders of magnitude. We have also included bead and fluid inertia in our simulation, which allows us to generate synthetic data with high frequency effects. As is well known, particle inertia causes oscillations and a ballistic regime at short time scales. If particle and medium inertia effects are taken into account the oscillations are damped by the Basset force, and the behavior is ballistic at the short-time regime.

Tuesday 2:45 Room 204 MF23

2-Dimensional mapping of dielectrophoresis-free AC electroosmotic flow

Jingyu Wang and H. Daniel Ou-Yang

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This paper reports a method to map the dielectrophoresis (DEP)-free AC electroosmosis (ACEO) flow field in the vicinity of conducting electrodes by isolating DEP from ACEO. The isolation is achieved based on the fact that the ACEO flow velocity is strongly spatially dependent whereas the DEP crossover frequency, the frequency at which the DEP force vanishes, is not. We used optical tweezers to position a single probe particle near the conducting electrodes, and measure the electrokinetic force on the particle in an AC electric field driven at the particle's DEP crossover frequency. This eliminated the effect of DEP and allowed us to calculate the flow velocity generated by ACEO. From this technique we created a two dimensional mapping of the frequency-dependent velocity field in the local window near electrode surface. Our experimental approach improves ACEO-based microfluidic applications, and allows future examination of the current electrokinetic theory on ACEO.

Symposium SA

Self-Assembling, Associative and Gel-like Systems

Organizers: Suzanne Fielding and Andrew Belmonte

Tuesday 3:35 Room 204 SA1

Rheology and adhesion of lightly cross-linked polymer gels

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Lightly cross-linked polymer gels are soft sticky materials with tunable properties making them excellent candidates for use in biomedical, microelectronics and other applications. We examine the relationships between various rheological and adhesive properties for a fluorosilicone gel manufactured by Dow Corning. This platinum catalyzed gel is cured at elevated temperatures resulting in a lightly cross-linked gel swollen by long chain silicone polymers which are covalently bound to the gel backbone structure. The commercially available materials are highly variable due to feedstock fluctuations. Materials are specified by the manufacturer based on hardness, which is reported as the force required to produce a specified indentation at a given rate. We determine the gelation time and shear moduli using oscillatory rheology. The degree of curing is measured in terms of extractable mass from the cured gel using methyl ethyl ketone. The modulus of the cured gel is measured over a range of temperatures using torsional rheology and the glass transition temperature is determined. Tack adhesion over a range of temperatures is also studied. We determine relationships between these rheological and adhesion properties and gel hardness as specified by the manufacturer.

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Tuesday 4:00 Room 204 SA2

Viscoelastic and mechanical behavior of hydrophobically modified physical hydrogels

Jinkun Hao and Robert A. Weiss

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Physical gels can be formed by interchain associations involving electrostatic interactions, hydrophobic interactions, hydrogen bonding or crystallizing segments. Because of the reversibility of these intermolecular interactions and the ability to rapidly respond to external stimuli such as temperature, pH or salt concentration, physical hydrogels can have much different properties from chemically crosslinked gels. In our research, the viscoelastic and mechanical behavior of physically crosslinked copolymer hydrogels synthesized from N, N-dimethylacrylamide (DMA) and 2-(N-ethylperfluorooctane sulfonamido) ethyl acrylate (FOSA), with varying FOSA content, were studied by rheological and static tensile tests. The strong hydrophobic association of the FOSA moieties in an aqueous environment produced core-shell nanodomains (~6 nm in diameter) that provided the physical crosslinks. These PDMA-FOSA hydrogels exhibited excellent mechanical properties. The modulus was 80 - 130 kPa, elongation at break was 1000 - 1600 %, and the tensile strength was ~500 kPa, depending on the FOSA concentration. Dynamic viscoelastic and stress relaxation experiments of this physical hydrogel and a PDMA hydrogel chemically crosslinked with N,N'-methylene bis(acrylamide) showed that the physical gel was more viscous than chemical gel, and it also displayed much greater stress relaxation. The physical PDMA-FOSA hydrogels were much more efficient at dissipating stress than the chemical hydrogels, which resulted in much higher strength and toughness, 4 - 6 MPa. This result was attributed to the extra energy dissipation mechanism provided by the reversible, hydrophobic crosslinks.

Tuesday 4:25 Room 204 SA3

Rheological properties of multifunctional cross-linked hydrogels

X Ye, J Ogle, and N Tonmukayakul

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Borate crosslinked guar gels are extensively used in oil field applications such as fracture stimulation of oil or gas wells, primarily for particle transporting etc. In contrast to such traditional monomeric cross-linkers, a novel pH-activated hydrogel has been developed which is made from mixing a synthetic polymer with reversible crosslinks with a natural biopolymer. The borate ions are evenly grafted onto the polymer chain and believed to be more efficient and showing better temperature stability. Potential economic benefit is thus recognized by using less amount of basic gel in fracturing applications. The rheological properties of these cross-linked gels using different molecular weights of the synthetic polymer have been characterized in terms of frequency, temperature, and polymer concentration. These are used to relate the macro flow behavior to its micro structure of hydrogels. Activation energies are obtained from applying time-temperature superposition principle in the terminal zone. Deviation of loss modulus at higher frequencies indicates another relaxation time scale associated to these aqueous gel systems, which can be used to explain the breakup rate of cross links. In addition, the reduced moduli are obtained by subtracting the base gel contributions and compared with previous works.

Tuesday 4:50 Room 204 SA4

Gelation of PHBV solutions

Ashish Lele, Prashant Patil, and Jyoti Jog

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PHBV, or Poly(hydroxybutarate-co-valerate), is a biodegradable aliphatic polyester having potential applications in packaging, biomedical and pharmaceutical sectors. A few reports have shown that solutions of PHBV in different solvents form gels upon cooling.(1-4) There are however no studies on the structure of the gels and kinetics of gelation. Here we report on the rheological studies of gelation of PHBV solutions of different concentrations in toluene under non-isothermal conditions at various cooling rates and under isothermal conditions at various degrees of undercooling. Early stages of gelation could be modeled by the Avarami kinetics, while at longer times gelation slowed down considerably followed by ageing. Results will also be presented on the microstructure of the gel.

1. Alessandro Turchetto, Attilio Cesaro, Thermochimica Acta 269/270 (1995), 307-317. 2. Deborah Fabri, Jiarui Guan, Attilio Cesaro, Thermochimica Acta 321, (1998), 3-16. 3. F. Bordi, C. Cametti, A. Cesaro, G. Paradossi, Polymer Vol. 37 No. 16, (1996), 3501-3507. 4. Andrij Pich, Nadine Schiemenz, Volodymyr Boyko, Hans-Juergen P. Adler, Polymer 47,(2006), 553-560.

Tuesday 5:15 Room 204 SA5

Using rheology to track growth kinetics of block copolymers in solution

Michael J. Heinzer, Stephen M. Martin, and Donald G. Baird

Chemical Engineering, Virginia Tech, Blacksburg, VA, United States

The manner in which solvent is removed during the solution-casting of block copolymer films has a significant influence on the polymer morphology in the final film, which in turn governs film properties. To better understand the ordering kinetics of block copolymers during the removal of solvent from a block copolymer film, dynamical mechanical measurements are used to track block copolymer phase separation in the presence of a neutral solvent. Iso-concentration rheology and small angle X-ray scattering experiments made at several concentrations during the solvent extraction process are compared to determine what structural changes (microstructure or domain evolution) account for changes in the rheology of a phase separating system. By considering the growth of different microstructures, the validity of using Avrami kinetics to interpret such rheology, particularly in terms of the physical meaning of the Avrami exponent, is studied. This talk will also introduce a new parallel plate fixture used for these experiments. The fixture consists of a porous bottom plate that allows for solvent removal from the top and bottom of the sample to alleviate concentration gradients and presents the possibility of tracking ordering in-situ as solvent is continually removed from the sample.

Symposium CR

Computational Rheology

Organizers: Randy Schunk and Juan P. Hernandez-Ortiz

Tuesday 1:30 Room 207 CR6

Non-monotonic stretch of isolated polymer chains in shear flow

Indranil Saha Dalal[1], Nazish Hoda[2], and Ronald G. Larson[1]
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We investigate the behavior of single polymer molecules in shear flows ranging from low to ultra-high Weissenberg numbers using Brownian dynamics simulations. A freely jointed polymer chain at a resolution of a single Kuhn step is represented by a bead-spring model with stiff Fraenkel springs that serve to mimic inflexible rods, and coarse-grained versions of this chain are modeled by the Cohen Padé approximation and the Underhill-Doyle model [J. Rheol. 49(5), 963-987 (2005)]. We observe that, for all chain lengths investigated, the average stretch in the shear flow direction increases monotonically with shear rate for low Peclet numbers ($Pe < 0.03$) and the chain stretch saturates at higher Peclet numbers ($Pe < 10$), as observed in previous work and in experiments with DNA chains. Here the Peclet number is defined as the shear rate multiplied by the rotational relaxation time of a single Kuhn step of the chain. Without excluded volume interactions, at even higher shear rates with $Pe > 10$, the stretch begins to decrease with increasing shear rate, in accordance with the similar simulations of Sendner and Netz [Eur. Phys. J. E 30, 75-81 (2009)]. The presence of excluded volume interactions offsets this tendency of the chain to shrink in size at high shear rates and, instead, the chain exhibits orientational "locking" effects at a highly extended state that leads to an increase in the mean stretch in the flow direction. Also, based on our simulations, we formulate a new model to explain the decrease of the chain dimensions in the gradient direction for intermediate shear rates ($0.03 < Pe < 10$) and its independence of the length of the chain. We observe that, for the case of polymer chains with 500 Kuhn steps, the predictions of mean stretch for both the coarse-grained models agree well with that of fine-grained chains at comparable Weissenberg numbers for shear rates low enough that the individual coarse-grained springs are not excited by the flow, but deviates significantly at higher shear rates.

Tuesday 1:55 Room 207 CR7

Diversity from uniaxial state and director incompatibility in nematic liquid crystals

Hossein Pourmatin, Amit Acharya, and Kaushik Dayal
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A numerical model is presented to simulate the diversity of nematic liquid crystal molecules from uniaxial state for any configuration, based on incompatibility equation of disclinations and the De Gennes order parameter tensor. A director incompatibility tensor is proposed to illustrate the defects in the model. This clears the ambiguity between the concept of biaxiality and defect in liquid crystals. Moreover, different examples of wedge defect have been studied to verify the effectiveness of director incompatibility tensor for different disclination strengths. At the end, an axisymmetric formation of molecules with a point defect in the center is studied to investigate the behavior of the proposed tensor for an infinite loop defect.

Tuesday 2:20 Room 207 CR8

Computational based study of suspension flow in a vane rheometer

Nicos S. Martys[1], Chiara F. Ferraris[1], William L. George[2], Steven G. Satterfield[2], and Marc T. Olano[2]
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Results are presented from a computational study of suspension flow in a three dimensional vane rheometer.The computational model is based on a Lagrangian formulation of the general Navier Stokes equations called smoothed particle hydrodynamics. The model is first shown to recover analytical predictions of torque vs. angular momentum for the simpler case of a continuum Newtonain fluid in a two-dimensional vane system. The detailed motion of aggregates for low and moderately high volume fraction is then illustrated for both cases of a Newtonian and a shear thinning matrix fluid. The time evolution of flow fields and stress fields are illustrated. For the case of dense suspensions, large correlated regions of stress that flare out radially, akin to stress chains, were observed. Linkage of the measured torque and angular velocity to the bulk fluids properties and comparison to experiments will be discussed.

Tuesday 2:45 Room 207 CR9

Dynamics of high-Deborah-number flows around a confined cylinder

Alexandre M. Afonso[1], Mónica N. Oliveira[1], Fernando T. Pinho[2], and Manuel A. Alves[1]
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The 2D flow around a confined cylinder is an important benchmark test-case in computational rheology [1]. From a numerical point of view, it is considered a smooth flow, due to the absence of geometrical singularities, such as the re-entrant corners found in contraction flows, another well-known benchmark flow for viscoelastic fluids. However, the flow past a confined cylinder also introduces significant challenges associated with the development of thin stress layers on the cylinder sidewall and especially along the centerline of the cylinder rear wake, imposing a limiting value to the critical Deborah number (De), for which steady numerical solutions can be obtained.

In this work, we present new results obtained for high-Deborah-number flows around a confined cylinder with a 50% blockage ratio for an Oldroyd-B fluid. These numerical results were obtained using the log-conformation formulation technique [2], in combination with a high-resolution finite volume method [3]. Converged simulations were obtained up to De=200, which is approximately two orders of magnitude higher than the limit achieved when using the classical extra-stress formulation. At those very high Deborah numbers a new and rich sequence of flow dynamic regimes was observed and mapped, showing the relevance of the front and rear stagnation points on the cylinder. In addition, the flow at high De is characterized by new elastic induced flow features, such as flow inversion near the cylinder walls due to elastic recoil. Preliminary experimental flow visualizations at the microscale show qualitatively some of these features, bearing in mind the differences associated with the three-dimensionality of the experimental geometry, with an aspect ratio of the order of 1.5.

References: [1] R.A. Brown, G.H. McKinley, J. Non-Newt. Fluid Mech., 52 (1994) 407. [2] R. Fattal, R. Kupferman, J. Non-Newt. Fluid Mech., 123 (2004) 281. [3] A. Afonso, P.J. Oliveira, F.T. Pinho, M.A. Alves, J. Non-Newt. Fluid Mech., 157 (2009) 55.

Tuesday 3:35 Room 207 CR10

On some matrix transformations applied to computational rheology

Alexandre M. Afonso[1], Manuel A. Alves[1], and Fernando T. Pinho[2]
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Computational rheology faces demanding challenges, such as the high-Weissenberg number problem (HWNP), which is characterized by a loss of convergence at moderately low levels of elasticity, quantified by the Weissenberg number (Wi). This numerical failure at Wi of the order of 1, is usually accompanied by numerical inaccuracies and lack of mesh-convergent solutions. Recent developments on the reformulation of constitutive equations for complex fluids, such as the logconformation [1] and the square-root-conformation [2] approaches, allowed further insights into possible solutions or, at least, alleviation of the HWNP.

In this work, a generic kernel-conformation tensor transformation [3] is presented for a large class of differential constitutive models. This kernel-conformation framework, in which several matrix kernel-transformation(s) families can be applied to the conformation tensor evolution equation, is generic and by itself does not guarantee a well-posed evolutionary numerical solution at high Wi. The numerical efficiency for defeating the HWNP is ultimately related with both the specific kernel function used in the matrix transformation, but is also related to the existence of mathematical singularities introduced either by the physical description of the flow or by the characteristics of the adopted constitutive equation. We also show that the log-conformation [1] and the square-rootconformation [2] approaches are two relevant particular cases of the kernel-conformation tensor transformation [3]. Simulations for the benchmark confined cylinder flow of an Oldroyd-B fluid provide an assessment of the merits and weaknesses of some tested kernel-functions.

References: [1] R. Fattal and R. Kupferman, J. Non-Newtonian Fluid Mech., 123:281-285 (2004). [2] N. Balci, B. Thomases, M. Renardy and C.R. Doering, J. Non-Newtonian Fluid Mech.,166:546-553 (2011). [3] A.M. Afonso, F.T. Pinho and M.A. Alves, The kernel-conformation constitutive laws, J. Non- Newtonian Fluid Mech., submitted (2011).

Tuesday 4:00 Room 207 CR11

A parametric study of two-layer polymer coextrusion

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Multilayer coextrusion of polymers is widely used in industrial processes such as film extrusion and wire coatings. Here, we use the commercial software POLYFLOW to simulate the extrusion of two polymeric layers: the inner layer being a viscoelastic fluid (a commercial LDPE, modeled with the Giesekus constitutive equation); the outer layer being an inelastic fluid (modeled as a generalized Newtonian fluid with a power law for the viscosity). The simulations are carried out assuming steady-state axisymmetric flow under isothermal conditions with incompressible materials. We are particularly interested in shape and the stresses that arise at the interface between the two layers, both inside the die and also at the die exit, as well as the overall die swell behavior developing in the process. The following parameters are studied with respect to their effect on the stresses at the interface: outer layer viscosity (as represented by the power law coefficients), the Giesekus model parameters, the pulling velocity of the extrudate, and wall slip, as well as the dimensions of the final product and the surrounding polymeric layers. As die geometry, we use a straightforward generalization of what has been used in the past [1] in single layer wire coating simulations.

[1] Ngamaramvaranggul, V., Webster, M.F.; *Int. J. Numer. Meth. Fluids* **2002**, *38*, 677-710.

Tuesday 4:25 Room 207 CR12

A numerical investigation of flow-type sensitive fluids

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This paper introduces stabilized finite element approximations for flow-type sensitive fluid flows. A quasi-Newtonian model, based on a kinematic parameter of flow classification and shear and extensional viscosities, is employed to represent the fluid behavior from pure shear to pure extension.Their major features are the viscosity function dependent of the flow type and the extra-stress tensor described by the generalized Newtonian model. The quasi-Newtonian fluid flows herein considered are approximated by a multi-field Galerkin least-squares (GLS) method in terms of strain rate, pressure and velocity. Due to the addition of residual-based least-squares terms of flow governing equations, the GLS method allows the use of simple combinations of finite element interpolations and remains stable even in flows subjected to high geometric and material non-linearity. The flow domain is a four-to-one abrupt planar contraction and the triple (D-p-u) is approximated by a combination of bi-linear Lagrangian interpolation for pressure, and bi-quadratic ones for the strain rate and velocity. The bi-quadratic interpolation for the tensor D assures an accurate representation of the flow classifier that depends on the first derivatives of D. For a relevant range of the Deborah number for such a problem (De from 0 to 0.6), three flow-type sensitive fluids are investigated: (i) a shear-thinning fluid; (ii) an extension-thickening fluid; and (iii) a shear-thinning and extension-thickening fluid. For all fluids, the distribution of the flow classifier is evaluated, capturing both extensional flow regions, in the contraction vicinity, and pure shear flows, far away from the contraction. The preliminary numerical approximations proved to be sufficiently stable and physically meaningful, encouraging in this way to deepen the numerical research of such a model.

Tuesday 4:50 Room 207 CR13

Computational modeling of high Deborah number flow and elastic instability in planar contraction geometry

Youngdon Kwon
School of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

Especially in highly nonlinear regime, elastic fluid such as polymeric liquid displays quite unique and various flow behaviors, drastically different from Newtonian one and often against our common intuition. Experiments, theoretical stability analyses and direct computational studies have been conducted to accumulate knowledge on this area of industrial as well as scientific significance. Computational modeling of these unique elastic flow phenomena, especially the purely elastic flow instabilities has been a challenging topic in rheology, which is far from complete resolution even after 50 years' elaborate research conducted by numerous scientists. In this work, we present and discuss the current status of understanding this problem recently achieved by the current author especially for the unstable contraction flow in 2D creeping flow asymptotics. In modeling we employ the essence of the mathematical stability results analyzed for constitutive equations, and then develop and implement appropriate computational algorithm for robust discrete continuation and fast time integration of governing equations. The algorithm demonstrates stable computation in highly nonlinear flow regime and the result exhibits symmetry breaking and oscillation of corner vortices in 4:1 contraction flow, which may be understood as purely elastic flow instability.

Tuesday 5:15 Room 207 CR14

Implementation of the wall slip boundary condition in a computational rheology code based on the finite volume method

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Although the no-slip boundary condition applies to most flows, there is experimental evidence for the existence of wall slip in many flows. Hence, for the sake of modeling accuracy it is important for computational methods to be able to consider this particular condition.

Most works on the implementation of the wall slip boundary condition concern Finite Element Method based approaches, while for the Finite Volume Method (FVM) the information is scarce. To fill this gap, we present two different numerical techniques for the implementation of linear and non-linear Navier slip boundary conditions, into a computational rheology code based on the FVM. The implementation is initially developed for channel flow and subsequently extended to geometries requiring non-orthogonal structured meshes and also to non-Newtonian fluid. A comparison between these new methods and the usual iterative process (update the boundary condition at the end of each iteration) is also presented, showing that for this new approach the convergence issues during the iterative procedure are solved.

With the proposed methodology and for the linear slip law, the implementation at the boundaries is fully implicit and convergence does not require relaxation, even when the slip coefficient is high. For non-linear slip laws, two alternative approaches for the numerical solution of the governing equations are also investigated: one requiring the solution of a transcendental equation at the boundary, and the other based on the linearization of the slip-stress vector relationship. The employment of the wall slip is illustrated with the numerical investigation of the flow in a 4:1 planar contraction of Newtonian and viscoelastic fluids described by the linear simplified Phan-Thien-Tanner rheological equation. While for Newtonian fluids the vortex size reduces with the increase of the slip level, for the viscoelastic fluid the size of the separated flow region remains approximately unchanged, but its shape is affected.

Wednesday Morning

Symposium PL

Plenary Lectures

Wednesday 8:30 Amphitheater A/B PL3

Reversibility, rheology, and nonequilibrium phase transitions in periodically sheared suspensions of non-Brownian spheres and rods

David J. Pine
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We explore the connection between reversibility and shear-induced ordering in non-Brownian suspensions of spheres or rods that are subjected to periodic strain. We find a number of remarkable results. First, we find that the shear-induced random collisions that usually produce diffusive dynamics can also lead to a non-equilibrium phase transition from a fluctuating (diffusing) state to a self-organized quiescent state (no diffusion). We also measure a time-dependent elastic component in the viscoelastic response even in the absence of Brownian motion. Interestingly, the time-dependent rheological data exhibit a universal scaling that is associated with a well-known class of non-equilibrium phase transitions associated with directed percolation. In suspensions of rods, we find that oscillatory shear flow tends to align rods perpendicular to the flow along the vorticity direction rather than aligning the system along the flow direction as is more commonly observed in shear flows. The orientational degree of freedom associated with the rods produces a time dependent control parameter that can drive the system through the non-equilibrium phase transition and can thus delay the ultimate transition to a fluctuating state. The basic features of these different behaviors can be understood in terms of a simple model in which hydrodynamics do not play an essential role.

Symposium SG

Rheology of Solids, Glasses and Composites

Organizers: Daniel J. Lacks and Sadhan C. Jana

Wednesday 10:00 Amphitheater A SG15

Time-temperature superposition in soft glassy materials

Rahul Gupta, Bharat Baldewa, and Yogesh M. Joshi
Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India

Time temperature superposition is a very powerful tool employed for those materials that are usually under thermodynamic equilibrium. Owing to temperature dependence of molecular relaxation processes, this tool can predict linear viscoelastic response of the materials beyond what can be measured by a rheometer at single temperature. Soft glassy materials such as concentrated suspensions, emulsions, pastes, etc. are known to be thermodynamically out of equilibrium and show time dependent evolution of their structures and physical properties. In these materials limited applicability of time translational invariance restricts use of Boltzmann superposition principle and time - temperature superposition in its conventional form. In this work we employ effective time theory and propose time - temperature superposition for soft glassy materials. We demonstrate successful application of this procedure to predict very long time and very short time creep and stress relaxation behavior of soft glassy materials.

Wednesday 10:25 Amphitheater A SG16

Swelling behavior of crosslinked rubber: Explanation of the elusive peak in the dilational modulus or swelling activity parameter

Ben Xu[1], Jinrong Wu[2], Xiaojun Di[1], and Gregory B. McKenna[1]
[1]Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States; [2]College of Polymer Engineering and Science, Sichuan university, Chengdu, Sichuan, China

Previous work[1] has shown that when handled properly, Frenkel[2]-Flory-Rehner[3](FFR) theory is an excellent model to explain swelling behavior with the exception of failing to describe the peak of the swelling activity parameter S ($S=\lambda\ln(a_c/a_u)$), or dilational modulus. This peak was first observed by Gee *et al.*[4] and has eluded explanations. In the present work, we explored the importance of fitting procedure to the isopiestic measurements data on the presence of the peak of S. We found the peak in S disappears when using a model based fit instead of the empirical or polynomial fits used previously. We think the "peak" in S is due to the experimental errors picked up by the fitting method. We also find that the

values of *S* (λ^2 approaches 1) are nonzero and increase as the crosslinking density increases, consistent with prior studies showing that Flory[5]-Huggins[6] interaction parameters of crosslinked and uncrosslinked rubbers are different. Finally we take model material parameters and show that adding less than 1% random error to the theoretical curves can lead to the peak in *S*. Importantly, this work shows that the Frenkel[2]-Flory-Rehner[3] is consistent with the swelling data and the resulted peak in *S* is an artifact of the fitting procedure.

1. G.B. McKenna and J.M. Crissman. J. Polym. Sci., Part B: Polym. Phys. 35, 817 (1997); 2. J. Frenkel, Acta Phys. USSR, 9, 235 (1938); Rubber Chem. Technol., 13, 264 (1940); 3. P. J. Flory and J. J. Rehner, Jr., J. Chem. Phys.,11, 521 (1943); 4. G. Gee, J. B. M. Herbert, and R. C. Roberts, Polymer, 6, 541 (1965); 5. P. J. Flory, J. Chem. Phys.,9, 660 (1941); 6. M. L. Huggins, J. Chem. Phys.,9, 440 (1941).

Wednesday 10:50 Amphitheater A SG17

Enhanced diffusion and rejuvenation in strained glassy polymers

Yongchul G. Chung and Daniel J. Lacks
Chemical Engineering, Case Western Reserve University, Cleveland, OH, United States

A glassy material is in a non-equilibrium state, and slowly moves toward the nearest equilibrium state. This process is called aging, and leads to changes in the material properties over time. Straining glassy materials have been postulated to 'rejuvenate' material properties (e.g., creep compliance), and recent experiments by Ediger and co-workers show that straining also leads to orders-of-magnitude enhancement in the dynamics (e.g., diffusion rates). We investigate this phenomenon using molecular dynamics simulations on a coarse grained model of polystyrene. Following strain, our results show that the dynamics of the material are accelerated, and become similar to the dynamics of equilibrium liquid near Tg. The enhancement in dynamic fades away with time and the behavior approaches that of the un-strained glass. The rate at which this enhancement fades away is shown to follow a powerlaw scaling, and is a function of both aging time and time-interval of measurement.

Wednesday 11:15 Amphitheater A SG18

The associated flow-rule and plastic deformation of transversely isotropic materials

Markus Hütter[1] and Theo A. Tervoort[2]
[1]*Mechanical Engineering, Eindhoven University of Technology, Eindhoven, Noord Brabant 5612AZ, The Netherlands;*
[2]*Department of Materials, ETH Zurich, Zurich 8093, Switzerland*

Plastic deformation of an anisotropic material depends on its orientation with respect to the loading direction. From a static elasto-plastic point of view, for transversely isotropic materials, this orientation-dependence of the yield stress is well-described by the yield criterion of Hill [1]. However, to capture anisotropic plastic deformation in a dynamic setting, e.g. using elasto-viscoplastic models [2, 3], a constitutive relation for the plastic strain rate is required. This is typically obtained by invoking the so-called "associated flow-rule," stating that the rate of plastic deformation is normal to the yield surface in stress space [2, 4]. This assumption allows the definition of a plastic strain rate from a static yield criterion, and is well established for isotropic materials.

This work presents a critical evaluation of the use of the associated flow rule to obtain the plastic strain rate for transversely isotropic materials using the yield criterion of Hill. It is shown that the plastic strain rate that is derived from the Hill criterion, using the associated flow rule, leads to the definition of an equivalent stress for yielding that is not consistent with the Hill criterion from which it is derived. This inconsistency is demonstrated by comparing both the Hill criterion and the yield criterion that follows from the associated flow rule, to experimental orientation-dependent yield stress data of pre-strained polycarbonate and polypropylene. Finally, we discuss an alternative procedure to describe finite elasto-viscoplastic deformation of transversely isotropic materials that is automatically self-consistent.

[1] Hill, R., Proc. R. Soc. London Ser. A 195 (1948), 281-297. [2] Rice, J. R., J. Mech. Phys. Solids 19 (1971), 433-455. [3] Hütter, M., Tervoort, T. A., J. Non-Newtonian Fluid Mech. 152 (2008), 53-65. [4] Hill, R., The Mathematical Theory of Plasticity, Oxford University Press, 1950.

Wednesday 11:40 Amphitheater A SG19

Simulation of mechanical properties of non-woven fabrics

Gun Woo Park and Kwang Soo Cho
Polymer Science and Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea

We suggest an algorithm which simulates mechanical properties of non-woven fabrics produced by spun-bonding process. Mechanical properties of non-woven fabrics depend on both physical properties of component fibers and the structure of the fabrics. The structure of the non-woven fabric may be simplified by the discrete orientation distribution of component fibers which are connected between regularly arranged bonding sites. We developed a model that describes motion of bonding sites which are coupled with neighbor bonding sites through connecting fibers. The equations of motion for the bonding sites provide what is the equilibrium configuration of bonding site under external loading on the fabrics. From this simulation we can find a way to connect mechanical properties of individual fiber with those of the non-woven fabrics.

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Wednesday 10:00 Amphitheater B SC29

Rheology of transient vorticity aligned structures in attractive colloidal suspensions

Chinedum Osuji and Ajay Singh Negi
Chemical and Environmental Engineering, Yale University, New Haven, CT 06520, United States

Shear rate jumps from high to low flow rates in an attractive colloidal suspension of carbon black particles in a non-polar solvent result in the formation of transient log-like structures aligned in the vorticity direction. Optical microscopy in situ with bulk rheology shows that the appearance of these aggregates is attended by an increase in the suspension viscosity. The viscosity shows a peak and then gradually recedes with passage of time under flow in concordance with the disappearance of the log-like structures. The time at which the viscosity reaches its maximum scales inversely with the shear rate applied to the system. This emergence of the peak in viscosity appears to be controlled by a critical strain and rescaling in these terms produces a common response across several different shear rates. Alteration of the attraction strength between particles by the addition of surfactant severely inhibits the structure formation. We present a simple model to account for these observations.

Wednesday 10:25 Amphitheater B SC30

Direct investigation of 3D suspension microstructural evolution

Bu Xu, M. Tharanga Perera, and James F. Gilchrist
Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, United States

Knowing the microstructure formation in sheared suspensions is key to understanding the rheological behavior of such systems. Stokesian dynamics simulations (e.g., Foss and Brady, J. Fluid Mech., 2000) predict anisotropies as a result of multibody hydrodynamic interactions. Thus far, few systems have elucidated data that can be directly compared to theory and computation. To determine the microstructure of near-hard-sphere microparticle suspensions, the local pair distribution function is presented based on experimentally obtained 3D particle positions using dynamic confocal laser scanning microscopy of fluids subjected to pressure-driven flow across various local volume fractions and shear rates. Evolution of structure from and isotropic distribution to that formed as a result of shear is elucidated. Silica suspensions of various pH values and electrolyte concentrations are investigated out of an interest on the competition between hydrodynamic and electrostatic forces. The results capture the evolution of suspension microstructure as a result of this competition. Explanation for this transition and its implication on suspension rheology is discussed.

Wednesday 10:50 Amphitheater B SC31

Nanoparticle organic hybrid suspensions: Structure and rheology

Samanvaya Srivastava and Lynden A. Archer
Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Sterically stabilized nanoparticle dispersions have attracted immense interest over the past few decades. Current understanding of these systems allows for a stable dispersion within only a narrow window in the grafting density and the swelling ratio (P/N) space. Here, we present first evidences of stable nanoparticle dispersion outside of the current parameter window using a new class of tethered nanoparticle systems termed as Nanoparticle Organic Hybrid Materials (NOHMs).

NOHMs are characterized by their high grafting densities and we report structure and rheology measurements of NOHMs with a silica core and polyethylene glycole (PEG) corona suspended in PEG oligomers at varying volume fractions. Definitive evidence of well-dispersed nanoparticles, leading to stable suspensions, are provided by structure characterization methods, which include electron microscopy and small angle X-Ray scattering. Scattering measurements also reveal the macro-scale equilibrium structure of these suspensions, which are in qualitative agreement with a recent theoretical study (Langmuir, 2010, 26, 16801).

Rheology results of these suspensions reveal a liquid-glassy transition at strikingly low core volume fractions. While their behavior is typical of Newtonian fluids at low particle loadings, high volume fraction suspensions display prominent stress overshoots in flow startups, indicative of elastic to viscous transition, and other characteristics of soft glasses. We also compare our experimental findings to the established SGR model and our systems can be used as model systems for understanding the jamming transition and other properties of soft glasses. Further, we elucidate the form of particle interactions and compare them with established models for spherical polymer brushes, and the inconsistency again points towards a revision in the current understanding of structure and wetting behavior of spherical polymer brushes.

Wednesday 11:15 Amphitheater B SC32

Structure and rheology of nanoparticle organic hybrid suspensions based on cube-shaped Fe_3O_4 cores

Rajesh K. Mallavajula, Lynden A. Archer, and Donald L. Koch
Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

Nanoparticle organic hybrid materials are a class of materials in which the nanoparticles are self-suspended in a polymer corona tethered to the particles. It has been reported previously that the flow properties of these systems can be tuned from simple Newtonian liquids to soft glasses by varying the particle size, particle shape, corona chain length and grafting density. Recently the effects of particle shape and topology on rheology and self-assembly have emerged as important topics for fundamental studies and for applications. This presentation focuses on the rheology, structure, and dynamics of oligomer- and self-suspended suspensions of cube-shaped nanostructures. Using a combination of theory, Brownian dynamics simulations, and experiments we show that the structure and rheology of suspensions of cubes are fundamentally different from those in suspensions of spherical particles at all particle volume fractions. Specifically, Brownian dynamics simulations are used to evaluate ordering and contact stresses between particles as a function of Peclet (*Pe*) number. Mechanical rheology, small-angle scattering, and electron microscopy experiments employing cube-shaped Fe_3O_4 nanoparticles with superparamagnetic and ferrimagnetic characteristics are used to investigate the effect of the shape on structure and rheological behavior over a comparable range of Peclet number.Observed phenomena such as disorder-order and shear thinning behavior are discussed with the help of theory and simulations.

Wednesday 11:40 Amphitheater B SC33

Particle chaining and chain dynamics in viscoelastic liquids

Alireza Mirsepassi[1], Derek Dunn Rankin[1], and Ali Mohraz[2]
[1]Department of Mechanical Engineering, University of California Irvine, Irvine, CA, United States; [2]University of California, Irvine, Irvine, CA, United States

The dynamics and the rheology of particulate suspensions in viscoelastic media are important in fields from materials science to life sciences. Particles can be used as fillers to change the mechanical, thermal, and electrical properties of polymer solutions or melts. Micron-sized particles are extensively used in paintings, coatings, and cosmetic products. Rheological properties of the background fluid can dramatically change the hydrodynamic interaction between particles and result in microstructucture formation and self-organization of particles in shear flows. Direct visualization of microstructure formation is carried out by confocal microscopy and bright field microscopy to quantify the dynamics of chaining in viscoelastic polymer solutions with different degrees of shear thinning. Effects of fluid rheology and particle size on anisotropy formation are investigated quantitatively.

Symposium FS

Non-Newtonian Flows and Stability

Organizers: Rob Poole and Fernando T. de Pinho

Wednesday 10:00 Founders Ballroom A FS10

Visco-plastic lubrication flows of viscoelastic fluids

Ian A. Frigaard, Sarah Hormozi, and Mark Martinez
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Multi-layer flows can be stabilised at the interface by strategically positioning layers of unyielded yield stress fluids. This technique, known as visco-plastic lubrication, has been demonstrated both analytically and experimentally for inelastic fluids. Here we present new results in which we establish the feasibility of the visco-plastic lubrication technique for viscoelastic multi-layer flows. We show results of experimental sequences using Carbopol and Polyethelene Oxide solutions as our base fluids. We also present results of an analysis using the energy stability method.

Wednesday 10:25 Founders Ballroom A FS11

Flow and displacement of viscoplastic fluids in eccentric annuli

K O. Olowolagba[1], K.V.V. N. Yerubandi[2], N Tonmukayakul[1], T Deawwanich[3], and D Q. Nguyen[3]
[1]Halliburton, Duncan, OK 73536, United States; [2]Halliburton, Pune, MH 411001, India; [3]School of Chemical Engineering, University of Adelaide, Adelaide, Australia

A pilot scale apparatus has been developed for experimental and visualization studies of the flow and displacement of viscoplastic fluids in eccentric annular channels. This phenomenon is relevant to the cementing operation in oil well completions, where drilling fluids are displaced from the annulus between the casing and the well bore by a series of spacer fluids and cement slurries. The test apparatus was designed to operate at various degrees of eccentricity and different angles of inclination to simulate a wide range of scenarios encountered in oilfield drilling and cementing operations. A special feature of the system is that the inner pipe can be rotated during displacement, allowing the effect of casing rotation on the performance of the displacement process to be studied. High speed video images capture the movement and evolution of the

fluid-fluid interface that clearly illustrate the effects of eccentricity, flow rate, cylinder rotation and fluid rheology on the displacement process. In addition, a method was developed for simultaneously determining the displacement efficiency by measuring the conductivity of the mixed fluid phase exiting the annulus. Pressure drop vs flow rate data are utilized for developing friction loss prediction models associated with single-fluid flow and two-fluid displacement in eccentric annuli. The results obtained are used to quantitatively assess the effects of various geometrical and operating variables on displacement efficiency. In particular, rotating of the inner cylinder during displacement was confirmed to be most effective in improving the displacement efficiency in highly eccentric annuli.

Wednesday 10:50 Founders Ballroom A FS12

Yielding behavior of a viscoelastic liquid driven by an initial shear stress jump

Yuriko Renardy[1] and Kara L. Maki[2]
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The dynamics of a viscoelastic liquid in parallel shear, driven by an initial shear stress jump, is investigated and shown to display thixotropy, yielding and unyielding behavior. The constitutive model is a combination of the partially extended convected model (PEC), modified to allow for a non-zero shear stress limit for large shear rates, and a Newtonian solvent. Thus, the concept of a yield stress is not built into the model. We assume that the ratio of retardation time to relaxation time is small, and perform asymptotic analyses of various time scales which emerge. The process of yielding reveals new solutions such as time-periodic solutions, in addition to the familiar steady shear flows. Such a yielded solution is used as an initial condition to study unyielding, together with a step-down in the applied shear stress. The subsequent dynamics again displays multiple time scales. Perturbation methods, in conjunction with direct computation of solution trajectories for the original full equations, shows novel transitions back to unyielded states. The commonly observed phenomenon of the hysteretic loop in the value of yield stress versus shear rate for steady shear solutions is also retrieved.

Wednesday 11:15 Founders Ballroom A FS13

Yielding behavior of entangled melts in complex geometries

Xiangyang Zhu and Shi-Qing Wang
Department of Polymer Science, University of Akron, Akron, OH 44325, United States

Recent particle-tracking velocimetric (PTV) observations have revealed strain localization either during startup shear beyond the stress overshoot or after a large step shear of entangled polymers (solutions and melts). The physical pictures leading to these decohesion events have been put forward [J. Chem. Phys. 127, 064903(2007); J. Rheol. 53, 1389 (2009)]. We envision similar failure behavior to occur in other forms of external deformation. In this presentation, we will discuss how entangled melts undergo strong deformation in pure shear and converging extrusion using the PTV method, and what critical condition is necessary to produce any uneven breakdown of the entanglement network.

Wednesday 11:40 Founders Ballroom A FS14

Planar oscillatory extensional flow of complex fluids

Chirag Kalelkar and Gareth H. McKinley
Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

We explore a nonlinear rheometric deformation termed Planar Oscillatory Extensional (POE) flow, which may serve as a useful model for investigating material responses to flow fields in which both extensional and shear kinematics occur simultaneously and periodically. For example, such tests may serve to elucidate the complex rheological response exhibited by a drilling mud as it flows within a well-bore, or by a fracturing fluid as it is forced through a porous rock formation. The POE deformation consists of periodic application of an exponential shear flow in a conventional cone-plate rheometer. This transient flow is a strong flow kinematically and can result in exponential growth of both the shear stress and normal stress difference with time. We use analytical and numerical solutions for the Oldroyd-B model to explore appropriate material functions for this large-amplitude periodic deformation history. We present results from experimental studies of dilute polymer solutions, viscoelastic gels and model drilling fluids subject to POE deformation and the observations are compared with a Newtonian calibration fluid subject to the same deformation history.

Symposium MB

Rheology of Polymer Melts and Blends

Organizers: Joao Maia and Avraam I. Isayev

Wednesday 10:00 Founders Ballroom B MB24

Large-amplitude oscillatory shear flow from the corotational Maxwell model

A. Jeffrey Giacomin, R. Byron Bird, Leann M. Johnson, and Adam W. Mix
Rheology Research Center, University of Wisconsin, Madison, WI 53706, United States

Using the single relaxation time corotational Maxwell fluid, we derive explicit analytical expressions for the first, third, and fifth harmonics of the alternating shear stress response in large amplitude oscillatory shear (LAOS). We also derive corresponding expressions for the zeroth, second, and fourth harmonics of both the first and second normal stress differences. These harmonics are found to depend upon just two dimensionless groups: the Deborah and Weissenberg numbers each of which causes non-Newtonian behavior. The form of the solution for the corotational Maxwell model in LAOS matches the forms of the analytical solutions for two molecular models for dilute solutions and one for concentrated solutions or melts. We also derive an analytical solution for the corotational Maxwell model after startup of LAOS. For this we find that both small and large amplitude cases approach a periodic limit cycle (alternance) at the same rate for both the shear stress response and for the normal stress differences. For molten high density polyethylene that is lightly filled with carbon black, we find good quantitative agreement with measured LAOS behavior when our analytical solution is superposed for multiple relaxation times.

Wednesday 10:25 Founders Ballroom B MB25

Linear vicoelastic rheology as a tool for the investigation of the chemical architecture of syndiotactic polypropylene

Naveed Amhad, Ilaria Di Rienzo, and Nino Grizzuti
Department of Chemical Engineering, Unversity of Naples Federico II, Naples 80125, Italy

Crystalline elastomers are olefin polymers or co-polymers, where the typical mechanical properties of crystalline materials (high rigidity and high stress-to-break) are associated with those of an elastomer (high deformability, high ductility). The above properties can be modulated by suitably changing the degree of order of the monomer distribution along the polymer chain. This has been made possible in recent years by the development of metallocene and post-metallocene homogeneous catalysts. In this work we studied the rheology of a particular class of crystalline elastomers, namely, a series of syndiotactic polypropylenes (sPP) of varying degree of tacticity. The linear viscoelastic properties of the different polymer samples were measured in both the melt state and below the melting temperature. The melt state experiments allowed the determination of the sPP plateau modulus and, as a consequence, of the molecular weight between entanglements. The experimental results show a strong, well defined correlation between the molecular weight between entanglements and the degree of tacticity of sPP. When performed below the melting temperature of each sample, linear viscoelastic measurements allowed for the determination of the early stages crystallization kinetics, which were also found to strongly depend on the architectural details of the polymer chain.

Wednesday 10:50 Founders Ballroom B MB26

An overview of models for unentangled and entangled dynamics

Alexei E. Likhtman
Department of Mathematics, University of Reading, Reading, United Kingdom

I will briefly describe my recent book chapter about models of polymer dynamics. I will start with models for unentangled dynamics and compare molecular dynamics simulations with many available single-chain models. In particular, I will show some detailed Rouse-modes analysis and detailed comparison of the static properties. I will then turn my attention to existing models for entangled dynamics, such as tube theory, slip-links models and chain in an array of obstacles. I will show the comparison of these models with molecular dynamics and highlight the conceptual problems standing on the way of further developments.

Wednesday 11:15 Founders Ballroom B MB27

Is it dilute enough? An examination of random walk polymer solutions

Sachin Shanbhag
Scientific Computing, Florida State University, Tallahassee, FL 32317, United States

We examine the percolation threshold concentration, c_p, at which overlapping Gaussian coils in a dilute linear polymer solution span the entire domain, and compare it with the overlap concentration c^*. When polymers are modeled as spheres of fixed radius equal to the radius of gyration, $c^*/c_p \sim 3$. We take the fractal nature of a random walk into account in the "fuzzy sphere model" by replacing the radius of gyration, with the average distance of the farthest entanglement point from the center-of-mass. For molecular weights up to 100 times the entanglement molecular weight, this leads to $c^*/c_p \sim 10\text{-}20$. However, Monte Carlo simulations using a more accurate "fuzzy ellipsoid model" which incorporates not only the fractal nature, but also the asphericity of random walks leads to $c^*/c_p \sim 6\text{-}12$ over the same range of molecular weights. This unexpected decrease is discussed.

Wednesday 11:40 Founders Ballroom B MB28

Analytical approach to discrete one dimensional barrier crossing for polymer nucleation

Matthew J. Hamer, Richard S. Graham, and Jonathan A. Wattis
School of Mathematical Sciences, University of Nottingham, Nottingham NG7 2RD, United Kingdom

In general barrier crossing problems are extremely difficult to simulate, our aim is to develop analytical techniques to accurately predict nucleation times of stochastic models through coarse graining. In particular, we look at the Graham-Olmsted polymer simulation which is a detailed multi-dimensional formulation, to make analytic progress we map this onto a one dimensional energy barrier, with nuclei volume the single variable. However the kinetics over this one dimensional landscape are still unknown, but we can extract reasonable approximations by throughly analysing simulation results. Given a fully defined one dimensional system, we can obtain an exact discrete expression for the average crossing time, from which a precise continuous approximation can also be produced. In the future, we intend to develop a model which includes nucleus rotation. To achieve this aim, we plan on breaking down this complex dynamic problem into a series of static ones.

Symposium SA

Self-Assembling, Associative and Gel-like Systems

Organizers: Suzanne Fielding and Andrew Belmonte

Wednesday 10:00 Room 204 SA6

Critical conditions for shear alignment of structured block copolymer systems

Vicki A. Cheng and Lynn M. Walker
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

Concentrated aqueous solutions of triblock copolymers with the structure PEOx-PPOy-PEOx form thermoreversible gels with an ordered micellar gel phase. Small angle x-ray and neutron scattering have been used to elucidate the specific close packed structures of these gels, which can vary from cubically packed spherical micelles to hexagonally-packed cylindrical micelles, depending on factors such as polymer concentration and temperature. Without manipulation these gels lack macroscale order; however, highly aligned crystalline structures are achieved under both steady and oscillatory shear conditions. Furthermore, this aligned crystalline state persists after cessation of shear. Alignment is detected through a drop in the magnitude of the moduli and this work is directed towards correlating the mechanical properties of the system with the conditions for shear alignment. In this work, a specific system (Pluronic F127) is probed at conditions where it is in a cubic phase. The block copolymer gel is probed using linear conditions and aligned using nonlinear oscillatory shear (high frequencies and amplitudes). The time and level of deformation required to align the system is quantified, and results suggest that there are critical times and deformation levels required for system alignment. These conditions for both neat and nanoparticle-loaded gel systems will be discussed.

Wednesday 10:25 Room 204 SA7

Deformation of multilamellar surfactant vesicles under shear flow

Angelo Pommella[1], Sergio Caserta[1], Vincenzo Guida[2], and Stefano Guido[1]
[1]Department of Chemical Engineering, University of Napoli Federico II, Napoli 80125, Italy; [2]Procter&Gamble, Pomezia Terme, Italy

Surfactant multilamellar vesicles (SMLVs) play a key role in the formulation of many industrial products, such as detergents, foodstuff, and cosmetics. In this work, we present the first quantitative investigation of the flow behavior of isolated SMLVs in a shearing parallel plate apparatus. We found that SMLVs are deformed and oriented by the action of shear flow while keeping constant volume, and exhibit complex dynamic modes (i.e., tumbling, breathing and tank-treading). A comparison with shear-induced deformation of unilamellar vesicle and droplets is also presented.

Wednesday 10:50 Room 204 SA8

Shear-induced structures in dilute polymer solutions

Rangarajan Radhakrishnan and Patrick T. Underhill
Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

Shear flow has the ability to induce the formation of structures in polymers when both attractive and repulsive interactions are present. These structures have been observed and are important for a range of systems including hydrophobic polyelectrolytes and associative block copolymers. A tumbling polymer in shear flow undergoes a cycle of compression and expansion which can lead to a set of coil-globule-coil transitions. These systems are particularly challenging to model because of the separation of time and length scales between the tumbling process and the scale of the attractive and repulsive interactions. We have developed a new coarse grained model of polymer solutions that show shear-induced structures and have performed Brownian Dynamics simulations. We will discuss how the effective solvent quality and balance of attractive and repulsive interactions alter the flow transitions. We have analyzed the importance of a balance of the rotational and elongational components of shear in forming these structures and the ability to form irreversible structures using flow.

Wednesday 11:15 Room 204 SA9

The interaction of topological defects with shear flows in thermotropic smectic liquid crystals

Sourav Chatterjee[1] and Shelley L. Anna[2]

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Some small-molecule liquid crystals form "smectic" or lamellar phases in which rod-like molecules align in 2D layers. Intermolecular interactions require the layers to remain at constant spacing, but they can bend easily in response to external fields. These mechanical properties lead to the formation of unique microstructures when initially aligned lamellar materials are subject to a shear field. In this talk, we examine microstructure formation and evolution in the thermotropic liquid crystal 8CB. We use a custom-built shear cell to apply steady and oscillatory linear shear flow, and we quantify texture formation using polarization microscopy. Nominally parallel layers of 8CB form topological defects known as parabolic focal conic defects that originate by an instability in which the layers undulate in order to relieve stress. Applied together, shear and dilatational strains lead to highly ordered square arrays of parabolic focal conic defects. Upon continued shearing, we observe that the ordered square arrays of defects move rigidly within the shear flow. The defects are positioned off-center in the cross-flow direction, and the defects do not fill the entire sample cross-section. However, the defect velocities are faster than expected if the defects are modeled as rigid objects translating in a Newtonian fluid. We modify an existing model for the amplitude of the layer undulations and show that energy minimization leads to a velocity profile that agrees well with the observed defect kinematics. Finally, we observe that application of large-amplitude oscillatory shear flow leads to annihilation of the arrays of parabolic focal conic defects. The annihilation of defects occurs by exponential decay of the number of defects as a result of dissipation of the elastic energy stored within the topological defects. These observations demonstrate the close coupling of the layer topology of lamellar liquid crystals with applied deformation fields.

Wednesday 11:40 Room 204 SA10

Shear induced gelation due to physical temporary networks in vinyl ester / carboxy terminated butadiene / styrene compounds

Tahmineh Mahmoudi, Gwang Seok Song, Dai Soo Lee, and Florian J. Stadler

School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju, Republic of Korea

The change of rheological properties of vinyl ester resin/CTBN/styrene on the amount of pre-shear is reported. These systems show a new type of shear thickening behavior, which is found by repeatedly measuring the viscosity function which itself is shear-thinning or by measuring at constant shear rate for a long time. However, by repeating the test in 20 cycles, the overall viscosity of the sample increases without reaching a steady-state. The change in viscosity from one cycle to the other is non-uniform. The physical reason for this novel shear-induced shear thickening is the formation of a temporary network due to hydrogen bonding, which is formed by shifting the balance between structuring and destructuring of the network consisting of H-bonded CTBN molecules. This is the first report of shear thickening in non-polymeric solutions, exhibiting a new rheological pattern.

Symposium PS

Polymer Solution Rheology

Organizers: Alexander M. Jamieson and Robert Weiss

Wednesday 10:00 Room 207 PS1

First particle tracking velocimetric (PTV) study of entangled polystyrene solutions

Gengxin Liu and Shi-Qing Wang

Department of Polymer Science, University of Akron, Akron, OH, United States

All previous PTV studies [e.g., Macromolecules 40, 8031 (2007)] have avoided the classic entangled systems based on polystyrene (PS) solutions, lending to the question of whether these PTV observations of polybutadiene (PB) based solutions are universal, capable of explaining the well known strain softening or ultra strain softening behavior that has been associated with the so called Doi-Edwards damping function or type C behavior [Osaki, Rheol. Acta 32, 429 (1993)] deviating from the DE function. To settle this matter, we examine the nonlinear responses of entangled PS solutions with PTV and show that much of strain softening is due to elastic yielding either occurring at the sample/fixture interface or in the bulk. Frequently, we observed non-quiescent relaxation that was not perceived in the literature fitting of the previous data (PS solution based) to the DE damping function, e.g., Fig. 7.16 in the Doi-Edwards book.

Wednesday 10:25 Room 207 PS2

Characterization of axisymmetric sphere-wall interactions in non-Newtonian fluids with particle image velocimetry (PIV)

Ian M. Klink, Daniel Eisenberg, and Ronald J. Phillips

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The fundamental problem involving the movement of a particle towards or away from a flat wall remains relatively under characterized in non-Newtonian fluids, as compared to similar problems in Newtonian fluids. Here we explore the qualitative and quantitative effects of fluid rheology on the axisymmetric sphere-wall interaction for three different fluids: a Newtonian fluid (5 wt% tetradecane in polybutene); a Boger fluid (0.30 wt% polyisobutylene, 4.85 wt% tetradecane, 94.85 wt% polybutene); and an elastic and shear thinning fluid (2 wt% polyisobutylene in polybutene). A range of sphere sizes and densities are explored in order to produce Deborah numbers in the range of 0.1 - 10, while maintaining small Reynolds and Stokes numbers such that the effects of non-Newtonian rheology can be isolated from inertia. The influence of non-Newtonian rheology is observed by comparing the velocities of spheres in each fluid, as well as by comparing the velocity fields around the spheres, as measured by particle image velocimetry (PIV). Sphere velocity profiles within a given fluid are also compared as the sphere moves towards, and away from the wall in order to observe irreversible non-Newtonian behavior.

Wednesday 10:50 Room 207 PS3

Using rheo-confocal microscopy to probe the entanglement-disentanglement transition (EDT) in DNA solutions

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Describing chain conformation and microscopic structures in presence of external deformation is an essential task in polymer rheology. Recently we integrated a commercial rheometer with a confocal fluorescence microscope (CFM) to directly image the conformational changes of stained DNA molecules and carry out simultaneous time-resolved velocimetric and rheometric measurements. This unique setup led to the development of a different approach in the study of entangled fluids [1-2]. We have identified a series of entangled DNA solutions that show homogenous and inhomogenous shear at high Wiesenberg number (Wi > 1.0). Fluorescent imaging was carried out on different entangled DNA solutions with concentrations ranging from 0.1 to 1.0% (with a wide range of entanglements per chain Z = 7-55) during shear. New experimental evidences of chain conformation in both startup shear and creep mode will be presented to further understand the molecular origins of EDT in shear thinning regime.

[1] Boukany, P. E.; Hemminger, O.; Wang, S. Q.; Lee, L. J. Phys. Rev. Lett. (2010) 105, 027802. [2] Hemminger, O.; Boukany, P. E.; Wang, S. Q.; Lee, L. J. J. Non-Newtonian Fluids. (2010) 165, 1613.

Wednesday 11:15 Room 207 PS4

The shear rheology of semi-dilute DNA solutions

Sharadwata Pan[1], D. A. Nguyen[2], P. Sunthar[3], Tam Sridhar[2], and J. R. Prakash[2]

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Extensive theoretical and experimental studies have been carried out so far to investigate the rheological properties of dilute polymer solutions and polymer melts in shear flow. However, a systematic experimental study to understand the rheological properties of polymer solutions in the semi-dilute regime is currently lacking in terms of understanding the influence of concentration, temperature and molecular weight. Knowledge of the rheological behavior of semi-dilute polymer solutions, which is characterized by significant hydrodynamic interactions and viscoelastic effects, is of crucial importance in a number of industrial and biological contexts. In this work, the shear rheology of linear DNA molecules in a wide range of molecular weights (25 - 165.6 kilobasepairs), temperatures and concentrations, has been investigated. DNA solutions have the advantage of being nearly perfectly monodisperse. Steady state shear viscosities, in both the dilute and semi-dilute regimes, have been determined. The dependence of the zero shear rate viscosity on concentration is observed to display universal behaviour that can be understood in the framework of scaling theories for polymer solutions. Further, the shear rate dependence of viscosity, at various temperatures and concentrations, can be collapsed onto master curves when interpreted in terms of a concentration dependent Weissenberg number. The material functions obtained in this work will provide benchmark data that are useful for the characterization of these industrially important systems, and for the validation of theoretical studies.

Wednesday 11:40 Room 207 PS5

The role of coil-stretch hysteresis in the capillary breakup of dilute polymer solutions

Ranganathan Prabhakar[1] and Siddharth Gadkari[2]

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Recent experiments on capillary breakup of solutions of flexible polymers have challenged the conventional notion of diluteness in such solutions: that intermolecular interactions are always weak when concentration c is significantly smaller than the critical overlap concentration, c*. It is observed that even when c << c*, the relaxation time τ_e extracted from the exponential decay of filament radius during the strain-hardening phase of breakup is a) very different from the "Zimm" relaxation time τ_Z obtained from small-amplitude oscillatory-shear measurments, b) can be *smaller* than τ_Z at very low concentrations, and c) exhibits a strong power-law dependence on concentration.

We attempt to predict this behaviour with a dumbbell model in which the conformation-dependence of the polymer friction coefficient also accounts for the influence of intermolecular hydrodynamic interactions between partially stretched molecules. We consider far-field interactions when molecules do not physically overlap. When overlap occurs, the blob-model is used to calculate the effect of screened interactions. The dependence of the equilibrium swelling of blobs on solvent quality is also accounted for. We model capillary breakup with a "zero-dimensional" stress-balance equation for the mid-filament plane, and suggest a method for correcting for the initial relaxation of filament profile prior to formation of a cylindrical thread.

Our results suggest that solvent-quality effects and coil-stretch hysteresis are crucial for explaining experimental observations. Model predictions compare well with experimental data for polystyrene-in-oligomeric styrene solutions, and we find that for these solutions, most of the observed "power-law" trend in the concentration dependence of τ_e is not due to semi-dilute solution behaviour.

Wednesday Afternoon

Symposium SG

Rheology of Solids, Glasses and Composites

Organizers: Daniel J. Lacks and Sadhan C. Jana

Wednesday 1:30 Amphitheater A SG20

Unique slow dynamics and aging phenomena in soft glassy suspensions of multiarm star polymers

Brian M. Erwin[1], Dimitris Vlassopoulos[2], Mario Gauthier[3], and Michel Cloitre[4]
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Below the yield stress, the rheological properties of soft glassy materials evolve slowly and endlessly with time. This is often rationalized in terms of aging and rejuvenation phenomena. The time spent at rest after preparation, the "age", plays the role of the longest relaxation time, providing a simple way to rationalize the mechanical response of many soft materials.

Here we show that this scenario is not universal and that aging can be influenced by local microscopic mechanisms. We study multiarm star polymer solutions, which are representative of the wide class of long-hairy particles. Stars interact through an ultrasoft repulsive potential. At contact, their partly interpenetrate by forming effective entanglements between the outer blobs. Star solutions exhibit unique history-dependent phenomena that are not observed in other colloidal or polymeric glasses. Terminal relaxation is reached at low frequencies and shear rates. Aging is associated with the slowing-down of terminal relaxation which occurs at lower and lower frequencies as time increases. The existence of a well-defined maximal relaxation time, which is short compared to the timescale over which it evolves, explains the time dependence of creep measurements, which vary with the total time elapsed after preparation and but not on the age. These results suggest that long-hairy particles such as star polymers belong to a new class of soft glassy materials.

Wednesday 1:55 Amphitheater A SG21

Yielding of hard and soft colloidal glasses under large amplitude oscillatory shear

Nikos N. Koumakis, Antreas Poulos, and George Petekidis
Institute of Electronic Structure and Laser, Foundation of Research and Technology, Heraklion, Greece

A colloidal glass at rest behaves like a soft solid, with the elastic modulus G' larger than the viscous modulus G" at all accessible frequencies. However, the same material will flow when subjected to a strain (or stress) that exceeds yielding. Beyond this shear-induced solid-to-liquid transition, colloidal glasses exhibit complex non-linear viscoelasticity that is still poorly understood. Here we study the yielding and non-linear viscoelasticity of model concentrated colloidal suspensions with hard and soft repulsive interactions using experiment and simulations. Large amplitude oscillatory shear (LAOS) is applied for various frequencies and the amplitude of oscillation is progressively increased to above the linear response regime, where the stress response ceases to be sinusoidal. LAOS experiments on hard sphere and deformable soft glasses are compared between each other with the purpose of contributing to the general understanding of the yielding processes in soft matter systems. With the addition of Brownian Dynamics simulations of concentrated hard spheres we gain insight on the correlation of stresses to microscopic properties during oscillatory shear by the analysis of particle displacements and structure. Elastic, plastic and viscous regimes within the period are identified with this microscopic information and then applied to the experimental systems. Small frequencies compared to the relaxation times of the systems are found to show a combination of elastic and plastic response within the period, while large frequencies show elastic and viscous responses. The deviation of the stress waveforms with respect to the first harmonic are determined at zero and maximum rate to reveal the relevant elastic and viscous contributions. Using such information, we comment on methods of looking at LAOS experimental results which are able to provide additional physical insight. Parts of this work are in collaboration with J. Stellbrink and J.F. Brady.

Wednesday 2:20 Amphitheater A SG22

Time evolution of colloidal glasses under constant stress

Pierre Ballesta and George Petekidis
FORTH, Heraklion, Greece

Colloidal glasses of hard sphere particles are model soft matter systems for the study of the glass transition. Similarly to other soft frustrated systems though they exhibits ultraslow dynamics which slow down with time (ageing) showing a departure from ideal glass behavior where a frozen out of cage motion is expected. Such behavior is related with dynamic heterogeneities, i.e. regions with enhanced cooperative particle motions observed by dynamic light scattering and microscopy but also indicated in linear and non-linear rheological tests. For example, whereas hard sphere glasses exhibit a yield stress plateau at low rates, when smaller stresses are applied a non-ideal response is detected through a prolonged creeping response. Here we investigate the behavior of glassy hard sphere suspensions submitted to such constant stresses. We show that even below the yield stress these suspensions present a finite albeit very high viscosity, whose value increases as the sample ages. At the same time the elastic modulus of our suspensions stays almost constant, while the loss modulus decreases with time. Moreover we simultaneously perform multispeckle dynamic light scattering (MSDLS) to investigate the evolution of microscopic particle dynamics under shear as a function of waiting time and relate it with the mechanical response of the system.

Wednesday 2:45 Amphitheater A SG23

Suspension-like rheology of crystallizing high-density polyethylene and time-hardening superposition

Peter C. Roozemond[1], Vincent Janssens[2], Peter van Puyvelde[2], and Peters W. Gerrit[1]

[1]Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands; [2]Chemical Engineering, Katholieke Universiteit Leuven, Leuven, Belgium

The rheology of crystallizing high-density polyethylene (HDPE) is investigated. Experiments on an HDPE were performed in a novel RheoDSC device, which allows us to perform rheometry and DSC simultaneously, thus measuring rheological properties and relative crystallinity on the same sample at the same time. Results agree quantitatively with simulations with the Generalized Self-Consistent Method for a suspension of elastic spheres in a viscoelastic matrix except for very low values of space filling (<5%), indicating that the rheological behavior of the crystallizing melt in the frequency range investigated is purely suspension-like.

The hardening behavior of the material is characterized in two different ways; a normalized rheological function and a time-hardening superposition master curve of rheological properties. An improvement is proposed to the procedure for performing THS that was previously used in the literature. Based on this procedure, a novel method for predicting the rheological properties of crystallizing melts is presented.

Wednesday 3:35 Amphitheater A SG24

Nonlinear viscoelasticity and extensional viscosity of polymer-layered silicate nanocomposites

Tanmay J. Pathak and Krishnamurthy Jayaraman

Michigan State University, East Lansing, MI, United States

The strain dependence of dynamic moduli in oscillatory shear has been reported for a variety of nanoparticle-filled polymer melts and elastomers-- see e.g. Cassagnau (2008). This paper investigates the strain dependence of dynamic moduli for different nanocomposites prepared with a maleated linear polypropylene copolymer and two distinct organoclays with different aspect ratios and surface treatments. Organoclay (A) had 27 wt% of a primary amine surfactant while organoclay (B) had 40 wt% of a quaternary amine surfactant. The effective aspect ratio of the layered silicates was determined from the relative viscosity to be roughly 100 and 175 in the two nanocomposite melts. The linear maleated random copolymer matrix had about 3 wt% ethylene, a melting point of 145C and molecular weight Mw=180,000. The dynamic mechanical tests on the nanocomposites were carried out at 155C in a TA-AR2000 rheometer. The thermal stability of structure in the two nanocomposite melts was confirmed with a small-strain time sweep over an hour. Three successive strain sweeps were carried out: the strain amplitude was varied from 0.5 % to 100% in every strain sweep at a fixed frequency of 1 Hz. The strain dependence of dynamic moduli reveals a distinct two-stage drop in the case of the nanocomposite with clay (B) which has the larger effective aspect ratio as well as the stronger interaction between polymer and organoclay. Successive strain sweeps take longer to merge with the first sweep for this nanocomposite. The recovery of storage modulus after a single strain sweep was also investigated with a time sweep at low strain and was much quicker for the composite with clay (B). The structural implications of these observations are useful for understanding the transient uniaxial extensional viscosity we have observed and reported for these melts with a rotary extensional viscosity fixture (EVF) on a TA-ARES rheometer.

Wednesday 4:00 Amphitheater A SG25

Structure and dynamics of polymer-grafted nanospheres in polymer melts

Daniel Kim and Lynden A. Archer

Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, United States

Colloidal particles functionalized with polymer brushes are widely employed for creating homogeneous polymer nanocomposites. The underlying benefits, such as mechanical reinforcement and reduction of polymer interfacial tension, are however largely confined to the so-called "wet brush" regime, in which the grafting density of the brush and the swelling ratio (P/N) of melt and graft molecular weight fall within well-defined ranges. Recent studies in our group have shown that oligomer-functionalized, self-suspended nanoparticles based on organic-inorganic hybrids, in which a core nanosphere is functionalized with a covalently attached corona and an ionically tethered organic canopy, are stably dispersed in polymer hosts outside the conventional wet-brush regime. This talk reports on the synthesis, structure, rheology, and interfacial properties of Polydimethylsiloxane (PDMS)-SiO2 hybrid nanostructures dispersed in a variety of polymer hosts. Transmission Electron Microscopy (TEM) and Small Angle X-ray Scattering (SAXS) are employed to critically evaluate the range of validity of literature phase diagrams deduced from theory of interacting brushes on planar substrates. By systematically studying hybrids with variable core particle size and tethered polymer molecular weights, we conclude that the curvature of the nanocores plays a heretofore unexplored role in stabilizing nanoparticles in polymeric hosts. Additionally, with the help of mechanical rheometry and atomic force microscopy measurements, we characterize the interfacial properties of thin nanocomposite films derived from these hybrid suspensions.

Wednesday 4:25 Amphitheater A SG26

Rheological expressions for the dispersion of organo-clay in a polymer

Brian L. Momani[1] and H. Henning Winter[2]
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Organically modified clay (layered silicate) is able to generate a soft physical gel when mixed onto an oligomer of end-functionalized ("sticky") macromolecules. In a freshly mixed sample, clay and polymer form a particulate suspension at first. But then the clay particles disintegrate into nanometer thick clay leafs and form a clay/polymer network with an internal connectivity that depends on the dispersion state of the organo-clay. The clay/polymer mixture was found to quickly pass through a physical gel point. Most of the structure evolved as a sequence of non-equilibrium states. The evolving dispersion was studied as function of temperature and time using rheological experiments and SAXS. Time-resolved mechanical spectroscopy was used as the macro-scale probe while SAXS served as the probe for nano-scale structure. The fully exfoliated clay structure served as reference for a rheological definition of the degree of dispersion. The exfoliation rate is highly temperature dependent as is the time-dependent degree of dispersion of the resulting nano-composite. The clay concentration was 8wt%. We acknowledge the support of the Petroleum Research Fund.

Wednesday 4:50 Amphitheater A SG27

Time/temperature evolution of the filler network in organoclay/polypropylene nanocomposites and application of the superposition principle

Riadh Zouari, Trystan Domenech, Bruno Vergnes, and Edith Peuvrel-Disdier
Centre de Mise en Forme des Matériaux CEMEF, MINES ParisTech, Sophia-Antipolis 06904, France

We investigate the rheological properties of a nanocomposite in small amplitude oscillatory shear. The nanocomposite is made up of an isotactic polypropylene (PP), organoclay and maleic anhydride grafted polypropylene used as compatibilizer to improve the dispersion of the clay. Samples are prepared in two steps: a masterbatch, obtained by melt extrusion, is diluted into PP using an internal mixer to obtain a well defined formulation. The investigation of the storage modulus evolution with time shows that this material is not stable: the microstructure obtained after continuous shear changes with time, due to the disorientation of the clay platelets and the build-up of a 3D network. This evolution of the nanostructure is evaluated by measuring the apparent yield stress. A two-step kinetics is evidenced, whose parameters directly depends on temperature. This time-evolution is generally assumed to violate the time-temperature superposition principle. We demonstrate that the time-temperature equivalence always exists if we use different annealing times for different temperatures, leading to the same nanostructure. The time-temperature equivalence evidences that the temperature does not induce any chemical change within the material whose properties remain governed by the same physical phenomena

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Wednesday 1:30 Amphitheater B SC34

Self-consistent particle simulation on flow and microstructure of colloidal suspensions

Jin Suk Myung, Kyung Hyun Ahn, and Seung Jong Lee
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Dynamics of stable and weakly aggregating colloidal suspensions were investigated by the self-consistent particle simulation method (SC), a new simulation algorithm that takes into account the interaction between the particles and suspending fluid. In this method, the fluid-particle interaction was taken into account by combining the microscopic particle dynamics and the macroscopic flow simulation. The flow field and the particle motion were coupled and solved self-consistently. Relative viscosity and microstructure of the stable suspensions under shear flow were investigated to validate the reliability of the proposed algorithm. The effect of the fluid-particle interaction was well represented in simulation on stable suspensions under rotating Couette flow. Non-homogeneous tangential velocity profiles and discontinuous shear rates demonstrated the existence of shear banding, which was found to originate from shear-induced alignment in the confined geometry. The microstructure and disturbed flow field of weakly aggregating suspensions under shear flow was also investigated. Although full hydrodynamic interaction (HI) was not rigorously taken into account, it successfully captured the macroscopic structure-induced flow field. We expect this study provide a deep understanding on dynamics of particle suspensions in complex flow field.

Wednesday 1:55 Amphitheater B SC35

Dissipative particle dynamics modeling of blood suspensions flowing in small tubes

Bruce Caswell[1], Huan Lei[2], and George E. Karniadakis[2]
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We have employed Dissipative Particle Dynamics (DPD) in a multi-scale model (MS-RBC) of healthy and of malaria-infected red blood cells (RBC). This model represents the cell membrane with hundreds or even thousands of DPD-particles connected by viscoelastic springs into a triangular network in combination with out-of-plane elastic bending resistance, and it captures the experimental mechanical behavior of single RBCs in a variety of static and dynamic tests. RBC aggregates (rouleaux) are modeled with the addition of inter-cellular adhesive forces. Without adjustment of parameters the calculated viscosities of model RBC suspensions are found to be in excellent agreement with measured viscosities for healthy blood both with respect strain rate and hematocrit(H). In this work we employ the model to calculate the flow of RBC suspensions in small tubes, (diameters 20-150 microns), and compare our results with experimental data. The viscosity results were derived from plane Couette flow simulations where both H and the velocity gradient were verified to be uniform across the gap, as expected. In Poiseulle flow the cross-stream stress gradient is well-known to induce radial migration of suspended particles. For fully developed flow of blood in circular tubes the main effects are the formation of a cell-free layer (CFL) at the wall and a peak in H near the centerline. Analytical theories have attempted to model tube flow of blood as a two-phase flow consisting of: a Newtonian plasma CFL, and a nonNewtonian fluid with uniform H in the rest of the cross-section. However, at H=0.3 simulations show that H is not uniform, and that in the larger tubes the velocity profiles are essentially parabolic. At the flow rates of these simulations aggregation has only minor effects when adhesive forces are set at healthy levels.

Wednesday 2:20 Amphitheater B SC36

Fractal model for viscosity of non-Newtonian liquid colloidal solutions

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The physical model for dependence of viscosity of colloidal solution on shear rate is proposed. The model is based on assumption that colloidal particles form aggreagates of fractal structure with sizes depending on shear rate value. As a result simple analytical formula was obtained for viscosity dependence both on shear rate and radius of fractal aggregate that describes experimental data with very good accuracy.

Wednesday 2:45 Amphitheater B SC37

Inertia matters

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We present the results of coarse-grained molecular dynamics simulations (LAMMPS) of particle mobility in hard-sphere colloidal systems with a background solvent. Simulations have been performed using Brownian Dynamics (BD) and Fast Lubrication Dynamics (FLD), an expedient to Stokesian Dynamics that breaks up the resistance tensor short-range lubrication and concentration dependent long-range isotropic terms. It is often considered that for colloidal systems of practical interest, inertial timescales are small enough to be ignored in determining particle mobility. The reasoning is that for particles in the µm size range, diffusive timescales can be many orders of magnitude larger than inertial timescales. To directly test this assumption, we make use of both inertial (explicit) and inertialess (implicit) langevin equations of motion for BD and FLD. The explicit form is a direct solution, including all force terms: inertia, resistance, interparticle interactions. The implicit form enforces force-balance, ignoring the inertial term ma; particle velocities are adjusted to maintain force balance. The advantage of an inertialess equation is that for sufficiently large particle sizes, a much larger timestep can be used. We find that the inertialess assumption leads to erroneous large early and late-time diffusivities at nonzero volume fractions $f>0.1$, an effect which increases with concentration. This is true regardless of the difference in the MD timestep used for explicit and implicit langevin equations. This presents a large problem in accurately simulating systems of µm or larger sizes, since the maximum possible explicit timestep is orders of magnitude smaller than a diffusive time. An alternate method known as telescoping is presented and shown to accurately predict late time diffusivities for colloidal systems. In this methodology, the inertial time is scaled to larger values without affecting diffusive timescales.

Wednesday 3:35 Amphitheater B SC38

Magnetorheological gels under magnetic field

Haining An
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Intelligent materials that respond to magnetic fields have gained considerable attention in the last decades. Magnetorheological (MR) systems include Magnetorheological fluids (MRFs), Magnetorheological elastomers (MREs) and MR foams. Compared to chemical cross-linked MR elastomers, physical gels are thermal reversible, easy to fabricate and their properties and morphology can be tuned by varying the gelator composition, molar mass and concentration. For those reasons, during recent years, there has been a growing interest to combine reversible physical gelation with magnetic properties. We recently reported on the linear viscoelasticity properties of tri-block copolymer physical gels containing pre-aligned magnetic particles [1]. At first glance, Magnetorheological Gels should behave similar to their elastomer counterparts (MREs). However, relaxations of the order of hundreds of seconds in storage and loss moduli are observed after imposing a step wise magnetic

fields. A plausible explanation may be the ability of soft gels to allow for a local rearrangement of the original particle network under magnetic field, likewise in fluids, while such rearrangement is much more difficult to occur in a hard elastomer. we show the a detailed investigation of the physically cross-linked MRGs where particle network still have some freedom to locally rearrange under magnetic field, as compared to MREs. Three parts of the result are shown: Transient dynamic response under stepwised magnetic field. Nonlinear rheology under large amplitude oscillation shear (LAOS). Cyclic hardening behaviour in the presence of external homogeneous magnetic fields when subject to cyclic shear.

1. H. N. An, S. J. Picken and E. Mendes, Soft Matter, 2010, 6, 4497.

Wednesday 4:00 Amphitheater B SC39

Experimental study on negative viscosity of a dispersion composed of spindle-like hematite particles in an applied magnetic field

Akira Satoh

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The spindle-like hematite (a-Fe_2O_3) particle has a unique characteristic that it has a magnetic moment which is weak but normal to the particle axis direction. Form this unique characteristic, we can expect that a dispersion of spindle-like hematite particles shows rheological and orientational properties in an applied magnetic field which are completely different from those of an ordinary magnetic suspension composed of ferromagnetic rod-like particles. Hence, we have been conducting a series of theoretical studies of these properties of a hematite particle dispersion and have first found an important result that this dispersion shows negative viscosity in the case of a magnetic field applied normal to the shearing plane in a simple shear flow. From this background, the objective of the present study is to experimentally verify the negative viscosity effect of a dispersion composed of spindle-like hematite particles. A glycerol-water based dispersion of these hematite particles was generated in order to investigate the rheological properties in the situation of an applied magnetic field. The main results obtained here are summarized as follows. The viscosity of hematite/glycerol-water dispersions for an applied magnetic field is smaller than that for no external magnetic filed. This characteristic of the negative viscosity arises more significantly with increasing strength of an applied magnetic field. On the other hand, the negative viscosity characteristic has a tendency to decrease for the shear flow governing more significantly. These properties of the negative viscosity are in qualitatively good agreement with those predicted by the previous theoretical studies. From these results, we make a conclusion that the negative viscosity effect predicted theoretically is verified by the present experimental study.

Wednesday 4:25 Amphitheater B SC40

Activated nanocage polymer electrorheological fluids

Ernest C. McIntyre and Peter F. Green

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We show that mixtures of small amounts (~1%) of sulfonated polyhedral silsesquioxane (s-POSS) nanocage with polystyrene (PS) microspheres and poly dimethyl siloxane (PDMS), exhibit significant electrorheological activity; the magnitude of the effect is comparable to that of conventional polymer ER systems. While the s-POSS/PDMS system is weakly ER active, the magnitude of the ER effect in the s-POSS/PS/PDMS mixture is more than an order of magnitude larger. The enhancement appears to be related to an interfacial interaction between the PS spheres and the s-POSS molecules, which possess permanent dipole moments. This effect is strongly dependent on microsphere size.

Wednesday 4:50 Amphitheater B SC41

Normal and shear stress correlation in field-activated fluids

Carlos S. Orellana and Heinrich M. Jaeger

The University of Chicago, Chicago, IL, United States

We measured the correlation between normal and shear stress on field-activated fluids. On a model giant electrorheological fluid we found a non-trivial strain dependent correlation between normal and shear stress that is affected by the boundary conditions. We show the amount of confinement on the system is critical to achieve a high shear stress response. In the magnetorheological case, the shear stress response is correlated to the positive normal stress on the plate, but not entirely to the magnetic field, making it possible to eliminate the field effect on the fluid by performing a fixed normal force measurement. In the regular electrorheological case, we find a competition between the negative normal stress due to the attraction of the plates and a positive normal stress due to shear, where the latter is correlated to the shear stress.

Symposium FS

Non-Newtonian Flows and Stability

Organizers: Rob Poole and Fernando T. de Pinho

Wednesday 1:30 Founders Ballroom A FS15

Linear stability analysis of streamwise vortices in shear flows of viscoelastic fluids

Alexander Morozov
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Recent work on transient growth in viscoelastic shear flows [1] suggests that even though these flows are linearly stable, a non-modal perturbation could be sufficiently amplified resulting in long-living transient disturbances. Similar to Newtonian shear flows, these disturbances take form of streamwise vortices.

Here we perform a linear stability analysis of the streamwise vortices superimposed on the steady shear flow. We find that this flow is linearly unstable towards 3D perturbations. In Newtonian case, this instability is known to play a crucial role in sustaining exact coherent structures [2] that dynamically organise the transition to turbulence. We discuss the possibility that similar structures exist in viscoelastic shear flows.

1. M. Jovanovic and S. Kumar, Phys. Fluids 22, 023101 (2010); 2. F. Waleffe, Phys. Fluids 9, 883 (1997).

Wednesday 1:55 Founders Ballroom A FS16

Transitional flow of a non-Newtonian fluid in a pipe

Ahmed Esamel, Chérif Nouar, and Alain Lefevre
LEMTA CNRS Nancy University, Vandoeuvre 54504, France

We present an experimental investigation of the transition to turbulence for non Newtonian fluid flows in a cylindrical pipe. Axial velocity profiles and turbulence intensity are measured using LDV system at different axial and azimuthal positions. It is shown that for shear-thinning fluids, the transition to turbulence takes place in two phases. In the first phase, the axial velocity profiles present an increasing asymmetry with increasing Reynolds number [Escudier and Presti J. non Newtonian Fluid Mech. 62 (1996)]. In a recent paper [A. Esmael and C. Nouar, Phys. Rev. E 77, 057302(2008)] a three-dimensional description of this asymmetry is provided. The results suggest the existence of a nonlinear state with a robust coherent structure characterized by two weakly modulated counter-rotating longitudinal vortices. Here, velocity fluctuations are studied, and it is shown that this state displays the salient feature of chaos, namely, randomly fluctuating motion excited in a broad range of spatial and temporal scales. This is the first experimental evidence of a weakly turbulent flow induced by the nonlinear dependence of the effective viscosity on the strain-rate of deformation, resulting from an interplay between inertia and the shear-thinning behavior of the fluid. Power spectra of velocity fluctuations decay following a power law with an exponent of -3. This suggests that, while random in time, the flow is rather smooth in space. The determination of the integral-scale shows that large-scale coherent structures are generated. Finally, the influence of the nonlinear variation of the effective with the shear-rate will be pointed out.

Wednesday 2:20 Founders Ballroom A FS17

Lifetime studies of localized turbulence in pipe flow of dilute polymer solutions

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At low Reynolds number, turbulence occurs in the form of localized "puffs" which have a finite lifetime and the probability of decay is exponentially distributed, characteristic of a memory less process [1-4]. In the present work, we extend the lifetime studies to dilute polymer solutions in pipe flow in the drag reduction regime [5]. Experiments have been carried out in a 900 D pipe of 4 mm diameter using different concentrations of polyacrylamide (PAAM) in water. The probability of a puff to decay strongly increases with the polymer concentration. This agrees with previous observations of transition delay. Our lifetime measurements allow us to quantify this process and to determine its dependence on the Weissenberg number.

References: 1) Björn Hof, Jerry Westerweel, Tobias M. Schneider & Bruno Eckhardt, 'Finite lifetime of turbulence in shear flows', Science, 2006,443, 59-62; 2) M Avila, A. P. Willis & B. Hof, 'On the transient nature of localized pipe flow turbulence', Journal of fluid mechanics 2010, 646, 127-136; 3) Hof B, A de Lozar , Kuik D J & J Westerweel , Repellor or attractor? Selecting the dynamical model for the onset of turbulence, PRL 2008101 (21) 214501; 4) D J Kuik, C Polema and J. Westerweel, 'Quantitative measurement of the lifetime of localized turbulence in pipe flow', JFM 2010, 645 , 529-539; 5) Toms BA "Some observations on the flow of linear polymer solutions through straight tubes at large Reynolds number", Proc. 1st Intl. Congr. Rheol. N. Holland, Amsterdam 2:135-41, 1948.

Wednesday 2:45 Founders Ballroom A FS18

Reynolds number variation in direct numerical simulation of polymer-induced drag reduction

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Large scale direct numerical simulation (DNS) results of turbulent drag reduction induced by injection of heavy-weight long-chain polymers in a Newtonian solvent are analyzed. The phenomenon is modeled for the 3d wall-bounded channel flow of a FENE-P dilute polymer solution. The flows considered have friction Reynolds numbers ranging from $Re_{\tau 0}$=180 up to $Re_{\tau 0}$=1000, and a constant friction Weissenberg number $We_{\tau 0}$=116 ensuring a high percent drag reduction of order 60%. The numerical simulations were undertaken with a hybrid massively parallel pseudo-spectral algorithm, making possible a high drag reduction regime together with higher Reynolds numbers than previously achieved.

We notice that the turbulence alteration by viscoelasticity is markedly Reynolds number dependent. This translates in a smaller percent drag reduction with increasing Reynolds number. The Reynolds number dependence is also visible on second-order statistics in a similar way as observed in Newtonian turbulence, i. e. the peak turbulence energy increases with Reynolds number and moves away from the wall. The well-known turbulence enhancing property of polymers remains anisotropic, irrespectively of the Reynolds number, the addition of polymer serving to enhance the streamwise normal Reynolds stress component (T_{xx}), while suppressing the other two normal components (T_{yy}, wall-normal) and (T_{zz}, streamwise). Yet, we notice that the reduction in T_{yy} and T_{zz} is less pronounced at high Reynolds number, especially towards the channel centerline.

Finally, the simulation results will be used to assess the 2 prominent long-standing explanations for the mechanism of polymer drag reduction proposed by Lumley (Ann. Rev. Fluid Mech., 1969) and De Gennes (Physica A, 1986). To achieve this goal the budget of elastic energy as well as estimates of the effective elongational viscosity will be considered.

Wednesday 3:35 Founders Ballroom A FS19

Slow flow of Boger fluids through model fibrous porous media

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As a means of studying elastic effects in flows through fibrous materials, we investigated flows of ideally elastic liquids through square arrays of widely spaced parallel cylinders. The arrays had solidities (solid volume fractions) of 2.5%, 5% and 10%, and the test fluids - one Newtonian fluid and two Boger fluids (PIB/PB solutions) - were driven downward by gravity through the three arrays at Reynolds numbers much less than unity. Pressure drop measurements were made over a range of flow rates to identify the onset and magnitude of elastic effects. Onset was consistently at a Deborah number of 0.5 and the flow resistance due to elasticity was up to several times the Newtonian value at the highest available Deborah numbers, around 4. Particle image velocimetry was used to map the velocity field in the interior of the arrays, which revealed, at high Deborah numbers, asymmetric velocity distributions and regularly spaced flow structures in the wake regions between cylinders. The structures in one wake region were offset spanwise to those in an adjacent region, forming a dovetail pattern. Flow kinematics and dynamics were analyzed using velocity data and measurements of N1 and extensional viscosity. The analysis indicates that the increased flow resistance due to liquid elasticity was related to shearing and not to extension, contrary to initial expectations.

Wednesday 4:00 Founders Ballroom A FS20

Three dimensional effects and stability of viscoelastic fluid flow past a confined cylinder

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In this work we present an experimental study of the 3D laminar flow around a confined cylinder with a 50% blockage ratio, and different aspect ratios, AR. This is the ratio between the cylinder length and diameter and the fluids tested are a Newtonian 40% w/w glycerol in water solution and a viscoelastic shear-thinning fluid (aqueous solution of polyacrylamide at 0.1% w/w). The influence of aspect ratio (AR = 2, 8 and 16) upon the flow characteristics is analyzed, at Reynolds numbers (Re) varying from creeping flow conditions (very small Re) up to the critical condition for the onset of vortex shedding. The experiments rely on visualizations of the flow patterns by streak photography and detailed velocity measurements using particle image velocimetry (PIV). The experimental results obtained with the Newtonian fluid are compared with numerical calculations, using an in-house finite volume code, and good agreement with the experiments is obtained.

For the Newtonian fluid the results show velocity peaks downstream of the cylinder for both inertial and creeping flow conditions, more markedly for higher AR. The intensity of velocity peaks increase with Re and they are located near the cylinder end-walls, at a distance of about one cylinder radius. Decreasing AR, the velocity peaks are smoothed and become quasi-parabolic.

For the viscoelastic fluid the results show the appearance of an elastic instability upstream of the cylinder, resulting in a progressive change of the location of the forward stagnation point, with the flow becoming increasingly asymmetric as De increases, but still under steady flow conditions, until a critical De is achieved and a second elastic instability occurs resulting in a time-dependent flow.

Wednesday 4:25 Founders Ballroom A FS21

Flow of thixotropic fluids past a confined cylinder

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A numerical study of the flow of a thixotropic fluid past a cylinder positioned between two parallel plates is performed, using a recently proposed constitutive equation. The equation is based on the upper-convected Maxwell constitutive equation for viscoelastic fluids, modified to accommodate structuring-level dependent relaxation time and viscosity. The structuring level is indicated by a structure parameter, which is governed by an evolution equation. The mechanical model is formed by the conservation equations of mass and momentum for incompressible fluids, coupled with the constitutive equation. The evolution equation of the structure parameter is purely hyperbolic, which certainly requires special care in its numerical approximation. The numerical approach is based on a four-field Galerkin least-squares formulation in terms of the extra-stress, pressure, velocity and structure parameter. The ratio of the channel height to the cylinder diameter is held fixed and inertia is neglected. For relevant ranges of rheological and flow parameters, the effect of thixotropy on the yielded and unyielded regions is obtained. The results reveal a strong interplay between the structure parameter evolution and the topology of yield surfaces throughout the channel. All the numerical results proved to be physically meaningful and in accordance with the related literature.

Wednesday 4:50 Founders Ballroom A FS22

Simulations of a sphere sedimenting in a viscoelastic fluid under the action of orthogonal shear

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During the fracture stimulation of oil and gas wells, suspensions of solids in polymeric solutions are pumped to help prop open the fracture. These solids, known as proppant, play an essential role in the hydraulic fracturing process. The performance of the proppant depends partly on the ability of the carrying fluid i.e. the polymeric solutions to support the weight of the suspended solids. These high density solids in the suspensions sediment in presence of gravity along with a shear flow in the orthogonal direction due to the motion of the fluid as they are pumped. Experimental data (Tonmukayakul et al., AIP Conf. Proc., vol. 1027, pp.791-793, 2008) has shown that both shear thinning and elasticity of the suspending polymeric solutions affect the settling rate of the solids. In some cases, the settling rate decreased which would make the proppant transport more effective. The mechanism of how elasticity of the carrying fluid affects the sedimentation velocity is not well understood. We use simulations of viscoelastic flow past a sphere with an applied shear in the orthogonal direction to study the phenomenon. We use the FENE-P dumbbell model as a model for the viscoelastic fluid. We find qualitative agreement with experimental data and predict the decrease in the settling rate. We additionally find that the rotation rate of the sphere increased in comparison to the case with a sphere in just the shear flow. Finally, we explain the mechanisms involved in the interactions of the viscoelastic fluid with the sphere which leads to this decrease in settling velocity.

Symposium MB

Rheology of Polymer Melts and Blends

Organizers: Joao Maia and Avraam I. Isayev

Wednesday 1:30 Founders Ballroom B MB29

A thermo-rheological study on the phase transitions of soft and hard thermoplastic polyurethanes

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Thermoplastic polyurethanes (TPUs) are multi-block copolymers consisting usually of hard and soft segments. Previous studies show that the thermodynamic incompatibility between hard and soft segments drives their microphase separation at low temperatures [1-3]. It is also known that the thermal history has a great effect on micro-aggregation structure and properties of TPUs. However, their rheological behavior is not well understood yet.

In this work two groups of commercial TPUs were investigated: one of them consists solely of isocyanate hard segments with diol chain extenders and the other one consists of hard segments of isocyanate with diol chain extenders and soft segments of diester with diol. Samples of extruded sheets were initially tested in steady and oscillatory shear. When temperature sweeps were performed at fixed frequency, hysteresis at lower temperatures in dynamic moduli was observed for both soft and hard TPU's. However, the hysteresis happens only in soft TPUs in the

loss tangent; in hard TPUs no hysteresis in loss tangent is observed. Moreover, it was observed that the hysteresis behavior is dependent on the amount of hard segments presents on soft TPU.

The phase transitions were also studied using extensional rheology and differential scanning calorimetry (DSC) with the thermal properties being measured during heating and cooling sweeps. The results indicate that the rheological response is more sensitive to the phase transitions than the thermal response, with the loss tangent being particularly good at differentiating between the structural evolutions of the soft and the hard TPUs.

References: [1] S. Cossar, D. Nichetti, N. Grizzuti, Journal of Rheology, 48, 691 (2004). [2] P. J. Yoon, C. D. Han, Macromolecules, 33, 2171 (2000). [3] S. Yamasaki, D. Nishiguchi, K. Kojio, M. Furukawa, Polymer, 48, 4793 (2007).

Wednesday 1:55 Founders Ballroom B MB30

Understanding melt index

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In plastics manufacturing, the melt flow index (MFI) is used as an indicator of rheological behavior when the more expensive and laborious determination of well-defined material functions is impractical. Specifically, the MFI is the mass flow rate in a pressure driven flow through a large, abrupt cylindrical contraction into a short tube performed under a standardized geometry, pressure drop and temperature. In this paper, we use an ANSYS POLYFLOW finite element model to explore the role of rheological properties on melt index. We uncover the meaning of melt index by calculating the mass flow rate in the melt indexer for a Newtonian fluid. We then explore the role of shear thinning by examining two generalized Newtonian models. Finally, we explore the role of melt viscoelasticity on melt index with a corotational Maxwell model. We present our results in dimensionless charts designed to help plastics engineers specify the MFI of a plastic for an industrial manufacturing process. A set of worked examples is included to show how to use the results.

Wednesday 2:20 Founders Ballroom B MB31

Combined synthesis, TGIC characterization, and rheological study of “H” polybutadienes, including the effects of synthetic impurities

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Long-chain-branched polymers are difficult to model rheologically, not only because of the complexity of their relaxation behavior, but also by their sensitivity to the presence of reaction byproducts, which are often impossible to completely avoid during synthesis, and can go undetected by conventional size exclusion chromatography. We address these problems here by using the most sensitive characterization method, namely temperature gradient interaction chromatography (TGIC), and applying it not only to the H-shaped polybutadiene (PBd) final product that we call "HA20B40," but also to the synthetic intermediate, an asymmetric star, both before and after purification of these samples. We measure the rheometry of all these materials and of these materials mixed with additional star and linear polybutadiene materials. In this way, we mimic the effect of impurities in the sample to test the ability of a rheological model, the "Hierarchical Model" to account for the effect of similar such impurities, which are detected by TGIC. Our modeling predictions for HA20B40 and its blends with star and linear polymers show very good agreement with measured rheological data, indicating that the modeling validation is successful for the symmetric H-shaped polymers. We then test the "Hierarchical Model" further using literature data for symmetric H PBds, for which the TGIC and experimental rheology data were published. We find that as long as the polymer composition is accurately determined, the "Hierarchical Model" can calculate the rheological behavior accurately. These methods can be used to help to identify the composition or impurities, which are almost always present at low levels at least in such topologically complex samples, and to test the ability of models to account for the effects of such impurities on the rheological behavior.

Wednesday 2:45 Founders Ballroom B MB32

Nonlinear shear rheology of entangled polymers measured with cone-partitioned plate

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Nonlinear shear rheological measurements are know to be challenging. A specialized cone-partitioned-plate fixture, first presented by Meissner, has been shown to help resolving, at least in part, the problem of edge fracture. We have adapted this idea for the ARES rheometer with temperature control and for very small amounts of sample. Reliable bulk shear flow data can be obtained in the temperatures range from -50 to over 200?C in a nitrogen environment. Extensive sets of start-up shear measurements on moderately entangled linear monodisperse polyisoprene (60 kg/mol) and polystyrene (182 kg/mol) melts are presented and discussed with focus on the Cox-Merz rule and the characteristics of the stress overshoot. The range of artifact-free data is extended by a decade in Weissenberg number (WiD). Results compare well with the limited experimental data available from the literature on monodisperse polymer melts. Furthermore, we show and discuss phenomenologically start-up data on model branched polymers (combs and dendritically branched). These branched polymers are much more prone to fracture compare to linear chains.

Wednesday 3:35 Founders Ballroom B MB33

Rotational rheometer with extended capabilities

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The main components of a rotational rheometer are the motor with its supporting bearings systems and the force measurement. In one design, commonly referred as CR (controlled rate or controlled strain), a displacement or speed is applied to the sample by a motor and the resulting torque is measured separately by the use of an additional measuring sensor. In a so-called CS (controlled stress) rheometer, an electrical current is applied and builds up a magnetic field, which produces an electrical torque. In such a design there is no separate torque sensor needed, since the torque signal is calculated from the motor current. The movement of the motor shaft is measured by an angular displacement sensor. Most CS instruments still employ a drag-cup motor like in the first CS instrument, the Deer Rheometer build in 1968. In 1995 a rheometer equipped with an electronically commutated synchronous Motor (EC-Motor) and Digital Signal Processor (DSP) technology was introduced. In the meantime the EC-motor technology is now for 16 years in various generations of instruments commercially available, making the technology with thousands of installations word wide well established. Since its first introduction significant improvements, due to the use of enhanced electronics, improved materials, and more sophisticated control mechanisms, have been implemented. Furthermore, based on the EC-motor technology a new technique is now introduced which represents a large step in rheometer development and extends the capabilities of a rotational rheometer dramatically. The aim of the paper is to describe the new technologies involved. Numerous application examples relevant for modern research on rheological topics mainly on polymeric systems are presented.

Wednesday 4:00 Founders Ballroom B MB34

Slip link simulations of entangled polymers under extensional/mixed flow: Dynamics of viscosity thickening

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A recent set of experimental data of the extensional viscosity of polystyrene melts obtained by Bach et al. Macromolecules 2003 revealed a failure in the available models for entangled polymers. The data shows an extensional viscosity thinning exponent of -0.5, in contrast to the value of -1 as predicted by the standard models. Another failure of the standard theories lies in the prediction of viscosity upturn. This experimental data showed no signs of upturn in viscosity for extensional rates of the order of inverse Rouse time of the chain (&tau$_R$$^{-1}$), whereas the standard theories predict the upturn in viscosity at extensional rates of the order &tau$_R$$^{-1}$. Interestingly, recent experiments by Sridhar et. al. confirm the -0.5 extensional thinning exponent but there data shows a viscosity upturn at extensional rates of order &tau$_R$$^{-1}$. Based on our extended slip-link simulations in planar extensional flow (Kushwaha et. al. JOR 2011), which predicts a thinning exponent closer to -0.5 than -1, we had proposed an explanation for the thinning dynamics that relied on disentanglement caused by the flow. In qualitative agreement with the experiments of Bach et. al., the simulations did not show any signs of upturn at extensional rates of order &tau$_R$$^{-1}$, but this issue was not examined in detail in the earlier work. In the present work, we aim to understand the dynamics behind the viscosity thickening and the parameters governing the upturn in the slip-link based framework. Based on our simulations, we show that the exact extensional rate of the viscosity thickening depends on the constraint renewal/release frequency, an input parameter to the mesoscopic model, which we believe should be obtained by a finer-grained simulation, such as molecular dynamics. We show that by varying this parameter we can vary the location of the upturn. Finally, we extend the model to model planar mixed flows using modified Kraynik-Reinelt boundary conditions.

Wednesday 4:25 Founders Ballroom B MB35

Stress versus orientation in the contributions to anisotropy in the thermal conductivity of polymers melts in flow

Jay D. Schieber, David Venerus, David Nieto, and Sahil Gupta
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Amorphous polymer melts exhibit anisotropic thermal conductivity when deformed. As suggested by van den Brule [Rheologica Acta, 28, 257-266 (1989)], a `stress-thermal rule' is observed, which is a linear proportionality between the stress tensor and the thermal conductivity. The proportionality constant is called the `stress-thermal coefficient' C_t. When this coefficient is made dimensionless by the plateau modulus G_N^0 of the polymer melt, a universal value of approximately 0.05 has been observed for polymers of different chemistries. Such a universality is unexpected, since thermal conduction is believed to occur by phonon transport, and be sensitive to small-scale or chemical properties. For example, the analogous stress-optic coefficient varies by a greater amount, and can even change sign. We therefore seek to examine the relative contribution of stress and polymer orientation to the thermal anisotropy. Using an optical technique, we measure the thermal conductivity of polymers with orientation, but no stress, and of polymers that have stress, but no orientation. We find that oriented (but unstressed) samples samples have a stress-thermal coefficient comparable to that flowing melts, and that stressed (but unoriented) samples have a stress-thermal coefficient of opposite sign, and whose magnitude is a factor of 100 smaller.

Wednesday 4:50 Founders Ballroom B MB36

Dielectric relaxation and rheology of bidisperse blends using the discrete slip-link model

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Dielectric spectroscopy is a well-known technique for studying structure and dynamics of polar material and is a useful compliment to conventional rheological method for investigating the relaxation properties of viscoelastic medium. In this work we look at dielectric and rheological properties for model bidisperse blends of linear polyisoprenes. We used the data published by Watanabe *et al.* [*Macromol.*, 2004, **37**, 1937-1951, 6619-6631], where the fraction of long chains varies from 0.05 to 0.5. The concept of dynamic tube dilation (DTD) was used in these papers to describe the data. The discrete slip-link model (DSM) is a more detailed model, and things like DTD are output from it rather then input into it. Therefore, DSM allows us to check the importance of the DTD concept. DSM shows good results in predicting rheological properties of bidisperse blends [R. N. Khaliullin and J. D. Schieber, *Macromol.* 2010, **43**, 6202-6212]. In this work we show that DSM can simultaneously predict rheology and dielectric spectroscopy data with the same set of parameters for the whole range of fraction compositions. Moreover, DSM allows us to reveal what assumptions prevent the tube models from successful description of data.

Symposium SA

Self-Assembling, Associative and Gel-like Systems

Organizers: Suzanne Fielding and Andrew Belmonte

Wednesday 1:30 Room 204 SA11

Bio-inspired metal-ligand crosslinks provide easy control of visco-elasticity of associative polymer networks

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Growing evidence supports a critical role for metal-ligand interactions in some of the unique properties of soft biological polymeric materials. For example, the strength of the coordinate bonds in Fe-catechol complexes combined with their capacity to reform after breaking has been proposed as a source of the self-healing in mussel adhesives. Inspired by the pH jump experienced by this marine bio-material during secretion, we have developed a simple method to control metal-catechol inter-polymer crosslinking and thereby tune visco-elastic properties of polymer networks. Exploitation of metal-ligand interactions to control material visco-elasticity could be a widespread strategy in Nature and a new opportunity in the polymer industry.

Wednesday 1:55 Room 204 SA12

Linear viscoelasticity and swelling of polyelectrolyte complex coacervates

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The addition of near equimolar amounts of poly(diallyldimethylammonium chloride) to poly(isobutylene-alt-maleate sodium), and vice-versa, results in formation of a polyelectrolyte complex (PE-complex) that precipitates from solution as a liquid coacervate containing roughly 70 wt% water. Conductometric titration and FTIR concludes that these PE-complexes are nearly charge-neutral, with similar stoichiometry regardless of the order of addition. Swelling and rheological properties are studied at different salt concentrations in the surrounding solution. The enhanced swelling observed at high salt concentration suggests the system behaves like polyampholyte gel with salt screening charge attractions. However, the weaker swelling at very low salt concentrations suggests the coacervate acts like a polyelectrolyte gel, with a weak net charge. Linear viscoelastic oscillatory shear measurements indicates that the coacervates are viscoelastic liquids and that increasing ionic strength of the medium weakens the electrostatic interactions holding the polyelectrolyte network together, lowering the relaxation time and viscosity. We use the time-salt superposition idea recently proposed [1]. This allows us to access timescale ranges otherwise inaccessible, and construct master curves for these soft materials.

1. Spruijt, E., Sprakel, J., Lemmers, M., Stuart, M. A. C., & Gucht, J. V. D. (2010). Dynamics in electrostatic complexes, 1-10.

Wednesday 2:20 Room 204 SA13

Structure-property relationships in conjugated polymer organogels

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Semiconducting, organogel networks of conjugated polymers represent a novel pathway towards the development of vertical charge transport in organic photovoltaic devices (OPVs). Conjugated polymers, such as poly(3-hexylthiophene) (P3HT), are known to form fibrillar structures when solvent quality is reduced. At high concentrations, P3HT will self-assemble and form gels with interconnected semiconducting fibers. The interconnectivity of these networks lead to a continuous, 3-dimensional path for charge transport which is ideal for the bulk heterojunction structure of OPVs. This talk will describe our recent systematic evaluation of the structure, mechanical, and electrical properties of these networks. A combination of rheology, admittance spectroscopy, and scattering techniques are used to fully characterize the P3HT gels. Through the combined use of rheo-SANS, and electro-SANS measurements we directly probe structure-property relationships in evolving P3HT gels. The results of this study will aid in the development and optimization of gel based OPVs.

Wednesday 2:45 Room 204 SA14

Linear and nonlinear viscoelastic behavior of triblock/diblock copolymer blends

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Thermoplastic elasticity in block copolymers is created by microphase separation on the molecular scale (5-100 nm), when both ends of an elastomeric polymer (B) are immobilized in hard domains of a thermoplastic polymer (A). As a result, although ABA triblock and AB diblock copolymer melts exhibit very similar phase behavior, their mechanical properties can differ substantially. In this study, we investigated the rheological behavior of blends of selected poly(DL-lactide-b-1,4-isoprene-b-DL-lactide) (LIL) and poly(DL-lactide-b-6-methyl-e-caprolactone-b-DL-lactide) (LML) triblock copolymers with low molecular weight IL and ML diblock copolymers. In particular, the nonlinear viscoelastic behavior was probed via start-up of steady uniaxial extension. A small amount of triblock copolymer had remarkably strong influence on the extensional behavior of these blends.

Wednesday 3:35 Room 204 SA15

Effects of gelation temperature on the rheology and microstructure of mozzarella type curd made from buffalo and cows' milk

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The rheology and microstructure of mozzarella type curds made from buffalo and cows' milk were measured at gelation temperatures of 28, 34 & 39°C. The maximum curd firmness (G') was obtained at a gelation temperature of 34°C in both types of bovine milk. The viscoelasticity (Tan d) of both curds were increased with the increasing gelation temperature. The rennet coagulation time was reduced with increase of gelation temperature in both types of milk. Frequency sweep (0.1-10HZ) was used 90 minutes after of chymosin addition, and both milk samples showed characteristics of weak viscoelastic gel systems. When both milk samples were subjected to shear stress to break the curd system at constant shear rate, 95 minutes after chymosin addition, the maximum yield stress was obtained at the gelation temperatures of 34°C & 28°C in buffalo and cows' curd respectively. The curd structure at different gelation temperatures was measured by using scanning electron microscopy and confocal laser scanning microscopy. Cows' curd was more porous than buffalo curd at same gelation temperature. This is may be due to differences in total solids and protein contents in both types of bovine milk. Porosity of curd was increased with the increase in gelation temperature in both milk samples. Key words: rheology, microstructure, buffalo, cows', gelation temperature, curd

Wednesday 4:00 Room 204 SA16

Flocculation efficiencies under various mixing mechanisms

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While suspension, slurries, and other particulate systems often contain distributions of hard-sphere like or weakly repulsive components, a host of environments exist in which particles clump together into aggregates or flocs of various sizes and morphologies. Flocculation is observed in clay-slurries and waste-water treatment facilities, during cheese production, and between algae in ponds and photo bioreactors. Under certain conditions, it is advantageous to accelerate the flocculation process through some kind of mechanical process. Harvesting of algae for use as a liquid biofuel is once such application. Two major barriers can exist to flocculation in systems of interest. Particulate components are often in the micron size range, with diffusion coefficients at or below 1E-9 m2/s. Additionally, the volume fraction of particles in the background solvent can be quite low, often below 0.0001. Brownian motion is therefore of little use as a means to bring particles together to form flocs. Other "mixing" methods can accelerate the rate at which particles encounter each other, including steady shear (couvette flow), turbulent mixing, and gravitational settling. Each method engenders its own cost. For the purposes of comparison, we use molecular dynamics simulations (LAMMPS) to study the flocculation kinetics of model particulate systems with realistic adhesive contacts based on a JKR framework under a variety of mixing mechanisms including steady shear, generalized white-noise, gravitational settling, and vortex flow. We then do a calculation of the energetic cost in using these mixing mechanisms. The goal of this study is to determine the optimally energy efficient means for accelerating flocculation kinetics. To this end we also consider floc morphologies and finite structural strength since there is a direct feedback between hydrodynamic forces acting on flocs and their size and shape.

Wednesday 4:25 Room 204 SA17

Correlating viscoelastic measurements of HPMC gels with the drug release from HPMC based matrix tablet

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Drug release from a hydroxypropyl methylcellulose (HPMC) based sustained release tablet can be a diffusion-dominant or erosion-dominant process depending on the characteristics of the drug and polymer, the formulation and the dissolution method and media etc. For HPMC, the viscosity and degree of substitution (hydroxypropoxyl and methoxyl) of the polymer have been shown to be the most important factors affecting drug dissolution. In this study, drug release from hydrophilic matrix tablets, composed of HPMC, was investigated for three different polymer batches. For the formulation studied, the drug release is dominated by polymer erosion. Differences in drug dissolution rate were observed although the batches were of the same pharmaceutical substituent (USP 2208) and viscosity (100 cps) grade. Such differences in drug dissolution cannot be explained by differences in the viscosity and degree of substitution of the polymer. Dynamic rheological measurements using a rotational rheometer were performed to characterize the HPMC gel samples. The storage modulus (G') of HPMC gels, which characterizes the gel strength, is shown to be correlated with the dissolution of the polymer. The results indicate that dynamic rheological measurements may be used to differentiate the HPMC lots and storage modulus (G') of the HPMC gel samples can be used as a parameter correlated with erosion-dominant drug release from hydrophilic sustained release formulations.

Wednesday 4:50 Room 204 SA18

Modulation of rheological properties in peptide-amphiphile based gels by tuning peptide head group interactions

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Peptide amphiphiles, short peptide sequences attached to a fatty acid tails, can self assemble into extended cylindrical micelles which entangle giving rise to a flexible hydrogel. The modular nature of peptide amphiphiles allows incorporation of features which can stabilize extended micelle structures, and add a variety of bioactive modalities. Peptide amphiphile based gels have intrinsically low modulus and limited tunability. In this work, hydrogen bonding of the peptide headgroup was studied as a method of stabilizing the micelles and thus increasing the modulus. Two approaches were used incorporating hydrogen bonding groups in the peptide backbone and side chains. In the case of the backbone hydrogen bonding gel, interactions of the head groups take place as result of secondary structure, namely ß sheet formation. In this system we show that the gel transition cue is the application of shear force and the mechanism of tunability is accomplished by changing the charged species present in the solution which affects the peptide's ability to transition in secondary structure. The available modulus range with this system spans G'= 10-100 Pa, making it well suited for a soft tissue cell matrix application, such as nerve regeneration. In the system where side chain hydrogen bonding is used, the gel transition cue is accomplished by raising the pH from acidic to physiological pH. The solution behaves as a weak gel at acidic conditions, and then effectively crosslinks through amino acid side chain hydrogen bonding to form very stiff gels at physiological pH. This system allows for tuning of the modulus by increasing the concentration and is able to span a range of G'= 100-10,000 Pa. This pH sensitive system is able to reach moduli significantly higher than traditionally self assembled peptide hydrogels and thus is well suited for a range of cell matrix applications, including muscle and bone tissue regeneration.

Symposium PS

Polymer Solution Rheology

Organizers: Alexander M. Jamieson and Robert Weiss

Wednesday 1:30 Room 207 PS6

Solvent effects on hysteresis in the coil-stretch transition

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The response of polymer solutions in elongational flow is important for many applications. One key feature of flexible polymers in elongational flow is the sharp transition from a coiled state to stretched state at a critical strain rate. It is important to understand how this transition is altered

by polymer-solvent interactions and conformation dependent drag. In theta solvent conditions, conformation dependent drag leads to hysteresis in the transition.

We have recently developed a model of polymer elasticity that includes solvent effects in a new way. Using Brownian Dynamics simulations of this model, we have predicted that some polymers could have dramatically different behavior due to solvent effects; the coil-stretch transition can be eliminated under some conditions. This new model allows us to better understand the importance of molecular flexibility and entropic elasticity in determining the flow response. We will discuss how our model can be used to understand how conformation dependent drag affects the coil-stretch transition in good solvents, comparing a dumbbell model and a bead spring chain model including hydrodynamic interactions between the beads.

Wednesday 1:55 Room 207 PS7

Analysis of temperature effects on drag reduction by polymer additives – rheometer experiments

Anselmo S. Pereira and Edson J. Soares

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The reduction of turbulent friction losses by addiction of high-molecular weight polymers in Newtonian liquids flowing in turbulent regimes has been extensively studied in many aspects such as numerical, experimental and theoretically since the phenomenon was first reported in 1948 by B.A. Toms. Along over 60 years, progress has been made to elucidate the complex physical interaction between the polymer and the turbulent dynamics. As a consequence of this, it is now quite well-known how the polymer concentration and molecular weight effects the drag reduction, although, many important aspects of the problem were not sufficiently analyzed yet, as the effect of temperature and pressure. An increase of the former parameter can reduce the relaxation time that is directly related to drag reduction. It suggests that temperature should be considered for an accurate analysis of the phenomenon. The contribution of the present work is an experimental investigation on drag reduction by addiction of high-molecular weight polymers in a turbulent Double-Couette flow produced by a rheometer endowed with an axial symmetric double gap sample holder. The focus of the work is on the temperature effect on the drag reduction and polymer degradation. The tests were carried out for polymeric solutions of polyacrylamide - PAM - and polyethylene oxide - PEO. A range of temperature from 20ºC to 50ºC was adopted. A maximum induced drag reduction of 26% was observed for PAM. No temperature effect was observed in the beginning of the tests, in which there is no degradation. Nevertheless, according to experimental results, the degradation mechanism is directly related to temperature and its increase reduces the polymer scissions for a fixed Reynolds number. We also analyzed the effects of concentration and molecular weight on both drag reduction and polymer degradation.

Wednesday 2:20 Room 207 PS8

Influence of excluded volume interactions on the force-extension behavior of flexible macromolecules: A Brownian dynamics simulation study

Mahdy Malekzadeh Moghani and Bamin Khomami

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Single molecule polymer studies are a valuable tool to harvest information about equilibrium and dynamic properties of polymeric systems. Recently single chain force-extension experiment for flexible macromolecules have shed light in the less explored area where tensile screening length is still larger than the monomer interaction range. In this range excluded volume effects are believed to contribute to the non linearity observed in the force extension behavior at small chain extension in these experiments. In fact theoretical studies based on scaling arguments predict extension (in the low extension limit) to be scaled with force to the power of ~2/3 in presence of excluded volume interactions.

Since most commercial polymers are generally flexible (small Kuhn length) and therefore excluded volume has a lingering effect up to a higher limit of extension, it's important to correctly understand these effects and be able to include them in polymer flow simulations accordingly. BD simulations provide a powerful tool to study polymeric systems or individual chains in equilibrium or under flow conditions. In this work in order to study the effect of excluded volume constraints on single chain extension behaviors Brownian Dynamic simulation of bead rod chain has been performed in the constant force ensemble with a new highly efficient parallel predictor corrector algorithm. Our results conform to the scaling behavior which is expected from self avoiding random walk chain. Moreover constant force ensemble simulation shows a non linear regime at high tensile screening length which can be used to develop new entropic spring force laws. Finally, single chain dynamics and rheological behavior of large Kramer chains ($O(10^3)$ Kuhn segments) under simple shear flow with excluded volume constraint and hydrodynamic interactions has also been compared with the free draining chain.

Wednesday 2:45 Room 207 PS9

Relating polymer dynamics to non-equilibrium statistical mechanics using the Jarzysnki equality

Folarin B. Latinwo and Charles M. Schroeder

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The study of complex fluids has benefited tremendously from the machinery of non-equilibrium statistical mechanics and other concepts in traditional physics. In the context of polymer dynamics, analytical tools such as renormalization group theory have been used to accurately predict (for example) the scaling exponent for a self-avoiding walk, while other approaches such as Fokker-Planck formalism have provided a starting point for kinetic theory and Brownian dynamics simulations of chain dynamics. In this work, we apply modern non-equilibrium statistical mechanics to polymer dynamics via the Jarzynski equality, which allows for calculation of free energy changes from non-equilibrium measurements. We utilize the Jarzynski equation to compute the free energy (an equilibrium concept) of a polymer molecule as a function of chain extension during far-from-equilibrium processes, such as chain stretching in strong hydrodynamic flows. To demonstrate the Jarzynski approach, we use Brownian dynamics simulations of discretized bead-spring chains to model dsDNA dynamics. Furthermore, we demonstrate that calculation of polymer free energy as function of chain extension allows for determination of chain force-extension elastic relations. Overall, this work shows that the formalism of non-equilibrium statistical mechanics may be applied to obtain information regarding chain elasticity from transient stretching trajectories of single chains in flow.

Wednesday 3:35 Room 207 PS10

Studies on strain-frequency superposition of large amplitude oscillatory shear: Comparison of experimental data with model calculation

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It was found that PEO aqueous solutions satisfy strain-frequency superposition (SFS) under large amplitude oscillatory shear (LAOS) flow. We calculate LAOS behaviors of several nonlinear viscoelastic models numerically and analytically. We found that some of nonlinear viscoelastic models satisfy SFS and others do not. For the calculation, we used relaxation time spectrum of polymer solutions which satisfy SFS. It is questionable that SFS depends on relaxation time spectrum or not. Unfortunately, experimental difficulty limits to check the effect of relaxation time spectrum. We will discuss this problem by use of model calculation.

Wednesday 4:00 Room 207 PS11

Investigation of rheological transitions and gel characteristics of methylcellulose in the presence of salts

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Many rheological additives have been investigated to allow formulators to create wide range of non-Newtonian characteristics to enhance the performance of personal care or pharmaceutical product or to enhance the ease of manufacturing process of these products. For example, a final product may require pourability and pumpability or rubbing and spraying which are determined by the rheological behavior of the final formulations. It is also known that many types of additives are incorporated into personal care or pharmaceutical formulations including salts, plasticizers, pigments, crystalline or noncrystalline drugs. The rheological properties of the final formulations with all of the additives are therefore key in determining the performance and processing conditions of these products. This study investigated thermo-gelation (hydrophobic interaction between partially/fully hydrated polymeric chains) characteristics of 7% methylcellulose (MC) at various salt concentrations of NaCl and $CaCl_2$. Both steady shear and dynamic results demonstrated that addition of NaCl has more pronounced gelation effect on 7% MC than that of $CaCl_2$. The rheological data is also correlated with thermal characteristic of these MC and salts.

Wednesday 4:25 Room 207 PS12

Abrupt shear thickening of associating polymer solutions

Ashish Lele, Indravadan Parmar, Manohar Badiger, and Prakash Wadgaonkar
Polymer Science and Engineering, National Chemical Laboratory, Pune, India

We have recently reported on the large and abrupt shear thickening of aqueous solutions of hydrophobically modified poly(N, N'-dimethylacrylamide-co-acrylic acid) using stress controlled rheology.(1) Specifically, we demonstrated that thickening occurs as a result of shear induced gelation at a critical shear rate. The gel so formed is metastable; the shear modulus of a gel of fixed polymer concentration can be 'tuned in' at will and the gel liquefies abruptly when a critical strain is reached. In this presentation we report on the influence of varying polymer concentration, ionic strength and temperature on the critical shear rate for thickening of the polymer solutions and the critical strain for liquefaction of the shear thickened gel.

(1) Ashish Lele, Aarti Shedge, Manohar Badiger, Prakash Wadgaonkar and Christophe Chasseneuix, Macromolecules 2010, 43, 10055-10063.

Wednesday 4:50 Room 207 PS13

Towards a redox-active viscosity switch via a copper ion-based metallosupramolecular polymer

Zheng Li[1], Adriane Miller[1], Stuart J. Rowan[1], Alexander M. Jamieson[1], and Kiril A. Streletzky[2]
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Metallo-supramolecular polymers (MSP), formed via self-assembly from a ditopic ligand through non-covalent metal ion-ligand binding are of current interest as a facile route to stimuli-responsive polymers. We have demonstrated the ability to generate multistimuli-responsive polymers from a ditopic macromonomer consisting of a 2,6-bis-(1'-methylbenzimidazolyl)-4-oxypyridine moiety (O-Mebip) attached to either end of a linear core. When the core is an oligoethylene oxide of DP 4, 5, or 6, the resulting MSPs form thixotropic gels via a novel colloidal gelation mechanism. When the core is polytetrahydrofuran of higher molecular weight, viscous solutions are formed. In the latter case, we explore the possibility to develop a redox viscosity switch based on the fact that O-Mebip forms a 2:1 complex with Cu(II) and a 2:2 complex with Cu(I). Thus by changing the Cu oxidation state in solutions containing copper ions and a ditopic ligand based on O-Mebip, switching between high and low molecular weight species should be possible at these two ligand to copper ion stoichiometric ratios. We test this hypothesis by investigating

the dependence of shear viscosity of MSP solutions as a function of ligand to metal ion composition, and metal ion oxidation state. Structural information on the MSP formed is obtained using static and dynamic light scattering, and small-angle x-ray scattering measurements. The influence on viscosity and MSP structure formation of macromonomer molar mass and solution ionic strength is explored.

Thursday Morning

Symposium AP

Award Presentations

Metzner Award Presentation

Thursday 8:00 Amphitheater B AP1

Modelling flow-induced nucleation in polymers

Richard S. Graham
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Flow-induced crystallisation (FIC) in polymers is a fascinating, externally driven, non-equilibrium phase transition, which is controlled by kinetics. FIC is also ubiquitous in industrial polymer processing. A fundamental understanding of FIC promises extensive control of polymer solid state properties, as virtually every property of practical interest is determined by the crystal morphology. However, modelling polymer FIC is extremely challenging due to the huge spread in relevant lengthscales and timescales. Furthermore, the most pronounced FIC effects are often seen at low undercooling. This temperature regime is especially difficult to simulate because the nucleation dynamics are controlled by extremely rare activated crossing of the nucleation barrier. We have recently been using a highly coarse-grained simulation algorithm for polymer nucleation. This has provided some encouraging comparisons with experiments. Nevertheless, an extended multiscale approach will be needed to simultaneously include the correct molecular physics, while also producing models that are sufficiently tractable for use in computational modelling of polymer processing. I will summarise current results and discuss methods of increasing the speed of barrier crossing simulations, along with techniques to map simulation algorithms on to non-stochastic models. Finally, I will also highlight some possible future methods to increase the physical detail of the underlying polymer nucleation model.

Symposium SG

Rheology of Solids, Glasses and Composites

Organizers: Daniel J. Lacks and Sadhan C. Jana

Thursday 8:40 Amphitheater B SG28

Thermally-activated shape memory behavior of fatty acid filled elastomeric ionomers

Shankar Kollengodu-Subramanian[1], Jing Dong[2], and Robert A. Weiss[1]
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Thermally-activated shape memory polymers (TSMP) are materials which demonstrate the ability to retain the temporary shape obtained by stretching the material above a critical temperature (Tc) followed by cooling under stress, as long as the material is kept below the Tc [1]. This unique property finds increasing interest in various fields of science and engineering for its ability of self recovery morphological healing [2, 3]. In the earlier work from our group [4], we demonstrated the ability to develop TSMP using a combination of fatty acids and ionomers with the fatty acid-ionomer interaction responsible for the temporary shape below Tc. Further, it was also demonstrated that by changing the fatty acid, it is possible to alter the critical temperature which can be exploited for various niche temperature based applications. In this work, we further characterize the TSMP using various thermal and rheological analyses to further understand these materials and the results are discussed.

References: 1. P. T. Mather, X. Luo and I. A. Rousseau, Annu. Rev. Mater. Res., 2009, 39, 445-471; 2. C. Liu, H. Qin and P. T. Mather, J. Mater. Chem., 2007, 17, 1543-1558; 3. A. Lendlein and S. Kelch, Augew. Chem. Int. Ed., 2002, 41, 2034-2057; 4. R. A. Weiss, E. Izzo and S. Mandelbaum, Macromolecules, 2008, 41, 2978-2980.

Thursday 9:05 Amphitheater B SG29

Effect of nano-particle shape on the linear and non-linear rheological properties of polymer nano-composites

Hojjat Mahi and Denis Rodrigue

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Effect of nano-particle shape on the rheology of polymeric nano-composites was studied by using two nano-particles having different shapes: spherical (nano-calcium carbonate ($CaCO_3$)) and platelet (nano-clay). Ethylene vinyl acetate (EVA) was used as the matrix and the nano-particle concentration was set between 0 and 15% wt. The samples were prepared first in a batch mixer in the melt state and scanning electron microscopy (SEM) showed a good dispersion in both cases. Then, a complete set of rheological tests including frequency sweeps, shear transients and uniaxial elongations was performed. Frequency sweeps showed that platelet particles have a stronger effect on the linear behavior of nano-composites than spherical ones. Also, the appearance of a solid-like behavior was much more pronounced for the platelet case. This is associated with the ability of platelet particles to create a network structure. Platelets particles can well interconnect and create a network structure leading to significant changes in the linear behavior. In transient shear tests, although both nano-composites presented a stress overshoot at high shear rates, the stress at yield was higher for nano-clay particles than for $CaCO_3$. This is also related to the network structures needing more stress to induce flow and to particle orientation effects. For uniaxial extensional flows, higher extensional viscosity was observed for platelet particles, but produced lower strain-hardening than spherical particles. Finally, nano-clay particles were found to reduce more the amount of extensibility (lower elongation at break) of polymeric chains than spherical particles.

Thursday 9:30 Amphitheater B SG30

Rheological and thermal properties of PET nanocomposites: The influence of clay chemistry and concentration

Abbas Ghanbari[1], Marie C. Heuzey[1], Pierre J. Carreau[1], Minh-tan Ton-that[2], and Weawkamol Leelapornpisit[2]

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Incorporation of layered phyllosilicates into polyethylene terephtalate (PET) can enhance various physical properties if a good level of nanoclay dispersion is achieved. Although for intercalated nanocomposites the gallery spacing of the silicate layers can be determined using wide angle X-ray diffraction (WAXD), little information can be obtained about the spatial distribution of the clay layers. On the other hand transmission electron microscopy (TEM) can reveal the state of clay dispersion and distribution within a polymer matrix; however this technique covers only a very small portion of the sample. In this work, PET nanocomposites containing nominal 2, 4, 6 and 8 wt% of organo-modified clays Cloisite 30B (C30B), Cloisite 25A (C25A), Cloisite 15A (C15A), Nanomer I.28E (N28E) and synthetic clay Somasif ME 100 (SM100) were prepared using a twin-screw extruder. Rheometry and differential scanning calorimetry (DSC) were employed in addition to WAXD and TEM. It was found that the gallery spacing of the organoclays within the PET matrix is almost independent of the clay chemistry and concentration; however the intensity of the peaks increases monotonically with silicate concentration. The PET nanocomposites containing organo-modified clays exhibit a shear-thinning behavior, while nanocomposites containing the unmodified clay (SM100) behave like the neat PET matrix. In addition, the complex viscosity of the PET nanocomposites increases monotonically with silicate concentration at low frequencies due to the formation of an interconnected or network-like structure. At high frequencies where the behavior of the matrix is dominant, a lower complex viscosity than that of the neat PET is observed due to PET degradation in the presence of the organoclays. The storage modulus increases at all frequencies with increasing clay loading. At high organoclay loading and low frequencies, the storage modulus is almost invariant with frequency which is an indication of a pseudo-solid like structure.

Thursday 10:25 Amphitheater B SG31

Structural stability of transparent conducting films assembled from single-wall carbon nanotubes purified by electronic type

John M. Harris[1], Ganjigunte Iyer[1], Jeffrey A. Fagan[2], Steven D. Hudson[2], Christopher M. Stafford[2], and Erik K. Hobbie[1]

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Strain-induced structural changes in thin polymer-supported membranes of purified single-wall carbon nanotubes (SWCNTs) are evaluated through the wrinkling instabilities that develop under uniaxial and isotropic compression. Nanotubes that have been purified by electronic type using density-gradient ultracentrifugation are assembled as surfactant-free films on prestrained polydimethylsiloxane (PDMS) substrates, and the strain response is measured using a broad range of techniques. The small-strain behavior is inferred from kinetic changes in the wrinkling topography during the slow drying of pre-swelled polymer supports. Our measurements reveal a remarkable degree of strain softening that couples strongly to the sheet resistance of the membranes through microscale anisotropy. By depositing comparable films on quartz, we use optical (UV-Vis-NIR) absorption spectroscopy to compute the London dispersion spectra of the purified materials, and from these we compute the attractive part of the van der Waals potential between nanotubes of identical electronic type. We find significant differences in the strength of the contact potential between metallic vs. semiconducting nanotubes, which in turn are evident in the modulus and yield strain of the films.

Supported by the NSF through CMMI-0969155.

Thursday 10:50 Amphitheater B SG32

“Boundary layer” in yield stress fluids : How does the butter slicer works

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In recent years there has been a strong effort for describing the rheological (bulk) behavior of yield stress fluids. The characteristics of the solid-liquid transition remain nevertheless poorly known. Here we focus on this phenomenon in the case of the relative displacement of a solid surface and a yield stress fluid. This question has a practical impact in various fields such as the adhesion of pastes over solid surfaces, the coating of cosmetic creams or gels, or the cleaning of tools in food industry or civil engineering. It also corresponds to the flow around a butter slicer as it goes through the material. We study this problem by displacing, along the plane axis, a thin, solid, rough plate through a wide volume of yield stress fluid macroscopically at rest. Our experiments with fluids of different structures show that, along the plane, a thin boundary layer of uniform thickness forms in which the material is in a liquid state while it remains solid outside. In addition, PIV experiments show that the velocity profiles in this boundary layer are self-similar and correspond to a decreasing exponential. More surprisingly the characteristic thickness of this boundary layer is not directly related to the rheological behavior of the material but significantly varies as a function of the fluid structure. The latter effect likely results from a complex process of solid-liquid transition around the plate tip. Finally this boundary layer thickness has a critical impact on the velocity reached by the plate for a given force.

Thursday 11:15 Amphitheater B SG33

Coupling of rheological and micromechanical techniques to determine strength and failure mechanisms of chemically modified TiO_2 and Al_2O_3 extrudates

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The use of rheometry provides valuable information on the physical properties of many materials; however, the understanding of failure mechanisms cannot be investigated by rheological methods. In this work, we study titania TiO_2 and alumina Al_2O_3 systems used for the fabrication of catalysts and high performance ceramics. A complete characterization starting from the rheology of the powders to the capillary analysis of the ceramic pastes has been carried out. In addition, compression strength and fracture of fired extrudates was explored by micromechanical test. Here, we present an innovative approach which combines the use of a new generation rheological apparatus with well established mechanical testing procedures. In particular, a rotational rheometer with micronewton force resolution and nanometer displacement resolution has been engaged to perform compressive crush testing on ceramic extrudates characterized by different scale of porosity and nanostructuring. The obtained force-displacement curves have been correlated with the formation and propagation of cracks in the material before the final fracture. In situ images captured by a microcamera and high resolution SEM micrographs of the extrudates acquired before and after failure complete this mechanical analysis providing a meaningful interpretation of the experimental data. A systematic study of chemically modified TiO_2 and Al_2O_3 powders with different initial particle size showed that pH greatly affects the microstructure and porosity of the pastes resulting in varying mechanical strength of the dried extrudates.

Thursday 11:40 Amphitheater B SG34

Modeling elasto-viscoplastic thixotropic yield-stress materials and apparent-yield-stress fluids: A unified approach

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[1]Department of Mechanical Engineering, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Rio de Janeiro 22453-900, Brazil; [2]Department of Mechanical Engineering, Universidade Federal Fluminense, Niterói, Brazil

A constitutive model for elasto-viscoplastic thixotropic materials is proposed. It consists of two differential equations, one for the stress and the other for the structure parameter, a scalar quantity that indicates the structuring level of the microstructure. In contrast to previous models of this kind, the structure parameter varies from zero to a positive and typically large number. The lower limit corresponds to a fully unstructured material, whereas the upper limit corresponds to a fully structured material. When the upper limit is finite, the model represents a highly shear thinning, thixotropic, and viscoelastic fluid that possesses an apparent yield stress. When it tends to infinity, the behavior of a true yield-stress material is achieved. The model is employed in different rheometric flows, and an excellent predictive capability is observed.

Symposium SC

Suspensions, Colloids and Emulsions

Organizers: Ali Mohraz and Matthew W. Liberatore

Thursday 8:40 Room 207 SC42

The effect of interfacial slip on the stretching, relaxation and breakup of a drop in a uniaxial extensional flow

Arun Ramachandran[1], Gary Leal[2], Kostas Tsigklifis[3], and Anshuman Roy[4]

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Using a numerical method based on the boundary integral technique, we assess the impact of interfacial slip on the dynamics of deformation and breakup of a single drop subjected to a uniaxial extensional flow under creeping flow conditions. Slip has a fourfold impact on the drop stretching, relaxation and breakup phenomena. First, when the capillary number is small, the steady deformation of the drop with slip is smaller than the no-slip result, and the difference increases with the viscosity ratio and the capillary number. Slip thus leads to larger critical capillary numbers beyond which the drop stretches continuously in the extensional flow. Second, for capillary numbers greater than the critical value, we find that the shape of the deformed drop for the same drop elongation is relatively insensitive to the slip coefficient, but the time required to reach this deformation is a strong function of the slip coefficient - slip slows down the deformation process. Third, the end-pinch mechanism of drop breakup leads to a different number and sizes of droplets with the inclusion of slip. Finally, slip causes the capillary instability mechanism of drop breakup to produce larger drops at faster rates relative to the no-slip case. In addition to the above results, we also show that slip moderates the viscosity and normal stress differences in a sheared, dilute emulsion. Our study has important implications in the area of blending of immiscible polymers, and indicates that the drop size distribution, which ultimately governs the material properties of the blend and composites prepared from it, is influenced strongly by interfacial slip.

Thursday 9:05 Room 207 SC43

Experimental study of drop separation in dense granular suspensions

Gustaf E. Mårtensson

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The controlled formation of droplets is of fundamental industrial and academic interest. The fluids of interest vary between industries and applications, and can include Newtonian and non-Newtonian homogeneous fluids, as well as complex fluid-particle suspensions. Although the break-up of fluid jets was first described in the late 19th century (Plateau, J. 1873, Gauthiers-Villars, Paris and Lord Rayleigh, 1879, Proc. R. Soc. 29:71), the field has continued to challenge researchers (Eggers, J. 1997 Rev. Mod. Phys., 69(3)). A novel jetting mechanism for highly viscous complex fluids that utilizes a helical viscous micropump to control the amount of fluid that is ejected by a piezo actuated mechanism has been developed and implemented by the authors. The ejected volume of fluid has been studied with respect to piezo voltage and pulse time of the piezo signal and the angular speed of the helical viscous pump. The ejected volume has been estimated from digital photographs taken of the droplet, as well as via 3D profilometry methods. It has been shown in the experimental jetting setup that the volume of a jetted deposit is only affected to a minor degree, of the order of 5% of the goal volume, by the chosen piezo voltage acting on the piston. This is also true for the chosen pulse time. The form of the ejected fluid droplet is affected by the pulse time only for relatively small volumes. Through imaging experiments, it has been shown that the speed of the ejected droplet has a nearly linear response to the piezo voltage. The area and estimated volume of the satellites formed at final pinch-off are calculated for the same parameter range as described above. The effect of the fluid's viscosity, represented by its dynamic shear modulus, G*, and its dependency on rate of shear, $d\gamma/dt$, on the ejected volume was also studied. The effect on the delivered volume was slight for the range of non-Newtonian fluids investigated, in spite of a strong shear-thinning behaviour.

Thursday 9:30 Room 207 SC44

Accelerated drop detachment in dense granular suspensions

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Laboratoire PMMH-ESPCI, Paris, France

We experimentally study the detachment of drops of dense granular suspensions. We compare our observations to the dynamics of pure oils matching the shear viscosity of the suspensions. In this way we show that at the beginning of the detachment process, the suspensions behave as an effective fluid characterized by its volume fraction. The detachment dynamics in this regime can be entirely described by the shear viscosity of the suspension. No increase of the viscosity under elongation is observed. At later stages of the detachment the dynamics become independent from the volume fraction. Rearrangements of the grains lead surprisingly to a behavior identical to the one of the pure interstitial oil, while particles are still present in the neck. The crossover to this regime is function of the grain size and the initial volume fraction. The final detachment is further accelerated. This acceleration is initiated by strong rearrangements of individual grains completely emptying the neck from particles. The cross over to this final regime is once again governed by the size of the particles and we observe coherently that it does not depend on the volume fraction of the dense suspension. We characterize the overall acceleration as a function of the grain size and volume fraction.

Thursday 10:25 Room 207 SC45

Relaxation of colloidal drop during drying via multi-speckle diffusing wave spectroscopy (MSDWS)

Jeong Yong Lee[1], Ji Won Hwang[1], Seong Jae Lee[2], Hyun Wook Jung[1], Jae Chun Hyun[1], and Sung Hyun Kim[1]

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During drying of suspension systems which contain micron sized particles in the liquid media, interesting time-dependent phenomena can be observed such as coffee ring, crack, and burst. In this study, fast motion and related relaxation dynamics of PS particles inside solvent under drying condition have been investigated using multi-speckle diffusing wave spectroscopy (MSDWS) method. The scattered light is detected employing the line scanning camera (multiple detectors) and then ensemble-averaged intensity correlation functions are interpreted from images taken by the camera. The movement of particles can be explained by the relaxation time of colloidal suspension which is typically proportional to the aging time. Also, the effect of initial concentration of suspension and particle size on the relaxation time has been examined.

Thursday 10:50 Room 207 SC46

Microstructure and rheology of bimodal PS latex/alumina-coated silica suspension

Jooyoung Lee[1], Seong Jae Lee[2], Kyung Hyun Ahn[1], and Seung Jong Lee[1]

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Some coating fluids such as cathode slurries used in manufacturing Li-ion batteries and Ni pastes in multi-layer ceramic capacitors include different types of particles to improve the performance of the product. In these liquids, the size of the particles is very different; one micron and the other nano-meter scale. It does not mean broad distribution, but distinctively two different sizes. These bi-modal suspensions show different fluid behavior compared to colloids of a single size since there exists additional interaction between two different particles. Small particles often form network structures. The interactions between unlike particles in composition, size, or surface potential may lead to complex phenomena such as hetero-aggregation, gelation, phase separation, and yielding. So, the control of microstructure and flow behavior of bi-modal suspensions is challenging in these industrial applications. In this talk, we will show the microstructure and rheological behavior of PS latex/alumina-coated silica suspension which was selected as a model fluid for bi-modal particle systems. The effect of concentration and surface potential of two different particles on fluid behavior will be discussed.

Thursday 11:15 Room 207 SC47

Effect of particle size on the dynamical arrest of model nanoparticle dispersions with short-range interactions

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The dynamical arrest of collodal dispersions encircles both academic and industrial challenges as material properties may drastically change upon arresting. A recent work by Eberle et al. (PRL 106(10) 2011) combined rheology, scattering techniques, and Monte Carlo simulations to measure the phase transition line at the dynamical arrest for a thermoreversible gel system (~30 nm). In their study, the gel line follows the percolation line and penetrates the gas-liquid coexistence curve at lower than the critical concentration. This finding indicates that phase separation does not precede gelation, disagreeing with the conclusion by Lu et al. for a colloid-polymer mixture system (Nature 453(7194) 2008). To extend our understanding, we use an identical thermoreversible gel system of different core particle sizes (~100 nm, ~300 nm) to study the effect of particle size on the dynamical arrest of model adhesive hard spheres. The model system is prepared by dispersing octadecyl chains-coated silica particles in n-tetradecane (J.Coll.Int.Sci 81(2) 1981). The brush layer promotes steric stabilization at high temperatures and crystallizes and induces a short-range attraction upon quenching the system (Langmuir 26(5) 2010). Characterizing the systems via rheology and light scattering techniques displays a very temperature-sensitive phase transition within 0.1°C and a power-law behavior in storage and loss moduli and in autocorrelation function at the vicinity of the gel temperature. Interestingly, a systematic relationship is seen between the gel temperature and the particle size when scaled by the amount of brush layer present in the dispersion. Also, small angle neutron scattering (SANS) is performed as a function of temperature and volume fraction to directly probe the microstructure at the transition. The SANS data suggests a qualitative agreement in the gel line for all particle sizes of interest tested, yielding lower values of the Baxter parameter as the particle size is increased.

Thursday 11:40 Room 207 SC48

Rheology of water coated glass beads dispersed in mineral oil as a model for hydrate slurry flow

Eric B. Webb, Matthew W. Liberatore, Carolyn A. Koh, Amadeu K. Sum, and E. D. Sloan

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Glass beads coated in water and dispersed in mineral oil will flocculate via capillary bridges. Adding just 1% water by volume to a solution of 20% glass beads dispersed in mineral oil dramatically increases the viscosity. Under shear, the glass bead aggregates may align, deform, break up, or further aggregate. Solid glass beads in a parallel plate geometry were a poor model system because of particle ejection at high shear rates and because of significant settling during experiments. Hollow glass beads in a concentric cylinders correct these issues. We convert the water shells surrounding the beads to hydrate by pressurizing our cell and decreasing the temperature. A unique magnetically-driven pressure cell with

peltier jacket is used to achieve high pressures (1500 psig) and low temperatures (0 °C). We observe the suspension viscosity change with time as hydrate nucleate, grow, aggregate, breakup, rearrange, and dissociate.

Thursday 12:05 Room 207 SC49

Rheology and morphology of hydrogenated castor oil crystals in aqueous dispersions

Dingzheng Yang[1] and Andrew N. Hrymak[2]
[1]Chemical Engineering, McMaster University, Hamilton, Ontario L8S4L7, Canada; [2]Chemical and Biochemical Engineering, Unversity of Western Ontario, London, Ontario N6A5B9, Canada

Hydrogenated castor oil (HCO) dispersions are widely used as the rheological modifier in paint, cosmetics and personal care products. Three HCO crystal morphologies have been observed, which we refer to by their geometric shape as fiber, rosette and irregular crystal. Due to the difficulty of obtaining samples with a single morphology, rheology studies of suspensions containing mixtures of the three morphologies in a non-Newtonian surfactant solution have been undertaken. The viscometry of dilute suspensions has shown that the magnitude of intrinsic solution viscosity follows the sequence of samples having a majority of a particular crystal morphology, i.e. fiber > rosette > irregular crystal. Huggins coefficients have been found to be the function of crystal morphology, indicating that a solution with a fractional distribution of 0.43:0.40:0.17 of fibers:rosettes:irregular crystals, shows the highest particle/particle interaction. The shear dependent viscometry of concentrated dispersions shows that Cross model fits well for the data at low volume fraction while a power law model fits well for the data at high volume fraction. The volume fraction dependent zero shear viscosity of concentrated dispersions has been found to be a function of crystal morphology with the highest zero shear viscosity found in fiber-rich systems and least zero shear viscosity for systems rich in irregular crystals. The linear viscoelasticity has been investigated, showing fibers and rosettes contribute more to elastic properties than irregular crystals.

Symposium FS

Non-Newtonian Flows and Stability

Organizers: Rob Poole and Fernando T. de Pinho

Thursday 8:40 Founders Ballroom A FS23

Shear banding in complex fluids

Suzanne M. Fielding
Physics, Durham University, Durham, United Kingdom

Following a brief introduction to the phenomenon of shear banding, I will discuss recent progress in modeling it theoretically. Polymeric, wormlike micellar and soft glassy materials will be discussed, in each case with particular attention paid to banding in transient scenarios such as the shear startup experiment. Time permitting, I will also make some remarks about instabilities in extensional flows.

Thursday 9:05 Founders Ballroom A FS24

Multiple banding of the VCM model for wormlike micelles under shear deformations

Lin Zhou[1], L. Pamela Cook[2], and Gareth H. McKinley[3]
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The VCM model was developed to provide a simple two-species description of many of the key features observed in the deformation-dependent nonlinear rheology of wormlike micellar solutions. It has now been studied in detail for several flow conditions including elongational flow, pressure-driven flow in channels and pipes, and Large Amplitude Oscillatory Shear (LAOS)). In all of these earlier studies the flow was assumed to be inertialess, so that kinematic boundary information propagates throughout the sample at infinite speed; the resulting rheological predictions are unique. In this talk, the predictions of the VCM model incorporating the effect of fluid inertia will be considered for two specific deformation histories; firstly, inception of steady state shear flow following a controlled ramp in the shear rate, and secondly LAOS. The presence of fluid inertia results in the transient propagation of elastic shear waves between the boundaries and, as a result of the interaction of these shear waves with shear-banding events, the model can predict multiple stable shear banding states in steady shearing deformation over a wide range of parameter space. Analogous non-unique steady states are observed in LAOS deformations in the limit of long time as the flow approaches a limit cycle. We develop a 'state diagram' showing the dependence of the multiple banding region on model parameters (elasticity, diffusivity) and on the initial conditions (i.e. the acceleration in the plate velocity). Three-band and four-band solutions can be observed and the temporal dynamics associated with their formation is explored. We investigate how the bulk rheological properties, including the shear stress and first normal stress difference, predicted by the VCM model are affected by fluid inertia and how the predictions vary with the magnitude of the single nonlinear parameter, ξ in the model.

Thursday 9:30 Founders Ballroom A FS25

A rigorous criterion for stability of viscoelastic flows

Michael Renardy
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It is customary to determine flow stability through computation of linearized spectra. While this criterion is well justified for the Navier-Stokes equations, it is not known whether it is always justified for the Euler equations or for viscoelastic flows. The lecture will present recently derived rigorous criteria by which the stability of creeping flows of nonlinear Maxwell fluids can be determined. In addition to the spectrum, one needs to examine the stability of certain systems of ordinary differential equations along streamlines of the base flow. These ordinary differential equations are linked to a short wave approximation of WKB type.

Thursday 10:25 Founders Ballroom A FS26

Viscoelasticity in thermoforming

Leann M. Johnson and A. Jeffrey Giacomin
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This analysis for thermoforming cones focuses on the manufacturing process speed and follows the method of Kershner and Giacomin for thermoforming with a nearly Newtonian melt. This analysis is expanded upon by deriving analytical solutions for both Upper Convective and Corotational Maxwell models. We have distinguished what happens before and after (free versus constrained forming) the melt touches the conical mold. Our results are confined to thermoforming cones, the simplest relevant problem in thermoforming.

Thursday 10:50 Founders Ballroom A FS27

Rinsing flows using non-Newtonian fluids

Travis W. Walker[1], Tienyi T. Hsu[1], Eric S. Shaqfeh[2], and Gerald G. Fuller[1]
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Rinsing flows refer to processes where a jet of one fluid (the jet fluid) is used to ablate a second liquid that coats a planar substrate (the coating liquid). Using an impinging jet of water to rinse coating fluids of varying rheology has been considered to understand the flow structures of the resulting hydraulic jumps qualitatively and quantitatively. We investigated the interactions of the two-fluid system during the transient growth of the flow profile, observing rheological dependencies on the magnitude, velocity, and topology. Various instabilities were also observed, including a flow profile dependency on the local viscosity ratio of the rinsing fluid to the coating fluid. Four classes of test fluids, each having approximately equal viscosities at low shear, have been chosen for this study: a Newtonian solution, a viscoelastic polymer solution, a Boger fluid, and a shear-thinning, inelastic colloid suspension. The presence of shear-thinning of the coating liquid influenced the overall velocity of the radial growth, while determining the geometry of the driving front. The dependence of these results on the local rheology was supported by experiments on Newtonian fluids of various shear viscosities. The presence of elasticity was seen to dampen the disturbances of the hydraulic jump, influence the overall jump height, and vary the radial growth of the jump.

Thursday 11:15 Founders Ballroom A FS28

Molecular migration in inhomogeneous shear flows

Andrew Schmalzer[1], Shihai Feng[2], Alan L. Graham[1], and Antonio Redondo[2]
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We report the results of non-equilibrium molecular dynamics simulations of pressure-driven flows of liquid argon in planar conduits. In the simulations, the conduits were ~60 atomic diameters across with ~25,000 atoms. Pressure driven flows were generated by applying a body force to each of the atoms ranging from 0.01 to 0.1 pN. When the flow rates are small, the liquid is on average incompressible and a parabolic velocity profile as predicted by incompressible creeping flow equations is observed. However, as the flow rates increase in isothermal pressure-driven flows, the molecules migrate to the low-shear-rate region in the center, and establish large density gradients across the channel under conditions that were assumed to be incompressible. The magnitude of the density gradients in the inhomogeneous shear flows increase monotonically with flow rate under conditions such that there is no significant slip at the walls. The migration of atoms to the channel center results in a higher viscosity in that region, and a blunted velocity profile that deviates from the solutions to the compressible Navier-Stokes equations that predict a parabolic velocity profile and a density that is only a function of the axial position. These isothermal flow results are distinctly different than simulations in which the walls were isothermal and viscous heating competes with the molecular migration. First, the two mechanisms balance each other and the density is constant across the channel width despite the higher temperature in that region. As the shear rate increases, the increasing temperature in the center of the channel eventually results in a density decrease in the center of the channel. When these same systems are subjected to linear simple shear flow at the same average shear rates, aside from localized wall-induced order, there is no variation of the average density across the channel. Hence this phenomenon is associated with the nonlinear shear in the pressure driven flows and not the magnitude of the shear rate.

Thursday 11:40 Founders Ballroom A FS29

Coarse-grain tunable dissipative particle simulation method for entangled polymeric systems

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Dissipative Particle Dynamics (DPD) [1] is one of coarse-grained level simulation techniques for soft materials that have been applied to a large array of systems such as Newtonian fluids, colloids, polymeric systems and so on. In DPD a conservative force parameter relates to the chemical potential, which, in principle, makes it suitable to study polymer blend, co-polymer and polymer nano-composites. Although many publications show the possibilities of the method, it has some drawbacks such as "bond-crossing" due to soft potentials, which affects to dynamics of polymer chains. Lahmar et al. [2] recently proposed a simulation DPD method coupled with Monte Caro (MC) method that provides Gaussian statistics and 3.2-power law on viscosity, which are reasonable, but shows unphysical properties such as non-Gaussian bond length distribution and no sign of entangled structures in the radius of gyration. In this work we present a modified DPD model that includes entanglement forces. The predictions by this method show 1) Gaussian statistics, 2) Gaussian bond distribution, 3) signs of entanglement effects in radial distribution function, 4) reasonable mean square displacement of entangled polymeric systems, which fits to tube model's prediction, 5) transition of linear viscoelastic properties (the storage modulus G' and loss modules G") from Rouse's behavior to reptation behavior with increasing molecular weight, 6) shear thinning, 7) shear and normal-stress difference stress overshoot upon start-up of shear at high shear rates.

References: [1] P. J. Hoogerbrugge and J. M. V. A. Koelman, Europhys. Lett., 19, 155 (1992). [2] F. Lahmar, C. Tzoumanekas, D. N. Theodorou and B. Rousseau, Macromolecules, 42, 7485 (2009).

Thursday 12:05 Founders Ballroom A FS30

Constitutive modeling of quasi-steady viscoelastic flow

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Steady-state non-Newtonian flow is most commonly modeled using the generalized Newtonian flow (GNF) model where the stress tensor is solely a function of the strain rate tensor. However, the GNF model cannot describe elastic effects such as normal stress differences; neither is it capable of simultaneously and correctly predict shear thinning and elongational thickening. In this study, a steady-state elastic flow model was developed to overcome these limitations. The residual elastic strain at the steady state was explicitly determined from the velocity gradient and used to express the stress tensor. The resulting stress tensor is only dependent on the objective part of the velocity gradient tensor, as adopted in the GNF model, and yet elastic effects can be accommodated. The case studies demonstrated that the new model is able to predict normal stress differences in simple shear and describe different rate dependency of viscosity in shear and elongation. At the small velocity gradient extreme, the present model correctly reduces to the Newtonian model. With more accurate determination of the residual elastic strain and better representation of the strain energy density function, this model may be further developed for modeling more realistic steady-state flow problems in complex geometries.

Symposium MB

Rheology of Polymer Melts and Blends

Organizers: Joao Maia and Avraam I. Isayev

Thursday 8:40 Founders Ballroom B MB37

Synthesis of PU/Expandable graphite nanocomposites with different hard segments ratio and evaluation of parameters affecting the phase separation by means of rheological techniques

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The main goal of the present work was to study the effect of loading EG (expanded graphite) on the morphology of the thermoplastic Polyurethanes. The samples varying in hard segment ratio (20%, 25%, and 30 wt %) and expanded graphite loadings (1, 2, and 3 wt %) were prepared by bulk polymerization. All the samples based on BD/MDI/PTMG were synthesized in two step method and in bulk state. XRD, RMS, and SEM techniques were used to analyze polyurethane and their nanocomposites microstructure. DSC, TGA, and DMTA experiments were also carried out to study thermal properties and tensile strength were evaluated to observe mechanical properties. Electron microscopy and X-ray scattering revealed an exfoliated microstructure which was found to be in agree with linear and nonlinear viscoelastic behavior of the samples. This was evidenced by the results obtained by thermal analysis. Results showed that use of expanded graphite caused reducing of phase separation. However, improvements by EG dispersion in tensile modulus were not as signi?cant. This may be because of flaws in the sheet structure formed during pyrolysis and oxidation used in exfoliation process.

Thursday 9:05 Founders Ballroom B MB38

How to obey the stress-optical rule without violating thermodynamics in slip-link models with virtual springs

Rudi J. Steenbakkers and Jay D. Schieber
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The rigid slip-link model (RSM) accurately predicts linear viscoelasticity [1] and flow [2] of polymer melts. In this single-chain mean-field model, entanglements move affinely with flow. The mobile slip-link model (MSM) adds fluctuations in their positions by connecting them, via virtual springs, to affinely moving anchors in the mean field [3]. We found the equilibrium primitive-path statistics of the MSM to agree better with atomistic simulations [4]. The free energy has contributions from the chain itself and from the confining potentials due to virtual springs. The latter are usually left out of the stress tensor expression because otherwise, first, the empirical stress-optical rule (SOR) is not obeyed, and second, the ensemble averaging involved in calculating the stress tensor seems to count chains more than once. However, when applying the virtual work principle, the virtual spring terms do not vanish [5]. Ignoring them thus violates thermodynamics. We resolve this issue by allowing the confining potentials to become anisotropic, inspired by Rubinstein and Panyukov's network model [5]. The novelty of our modified MSM is that the potential deformation is fully 3D, whereas their model is restricted to principal directions. In the variable space including the actual conformations of strands and virtual springs, as well as in a contracted variable space involving only mean conformations, we show that the virtual terms in the stress tensor cancel if the potential deformation is upper-convected. Thus the SOR is obeyed and multiple counting is avoided in a way that is physically reasonable and, more importantly, does not violate thermodynamics.

[1] R.N. Khaliullin and J.D. Schieber, Macromolecules 42, 7504 (2009), 43, 6202 (2010) [2] J.D. Schieber, D. Nair, and T. Kitkrailard, J. Rheol. 51, 1111 (2007) [3] J.D. Schieber and K. Horio, J. Chem. Phys. 132, 074905 (2010) [4] R.J. Steenbakkers and J.D. Schieber, SOR 82nd Annual Meeting (2010) [5] M. Rubinstein and S. Panyukov, Macromolecules 35, 6670 (2002)

Thursday 10:25 Founders Ballroom B MB40

Assumptions of the discrete slip-link model and their effect on non-linear rheology predictions

Marat Andreev, Jay D. Schieber, and Renat Khaliullin
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The discrete slip-link model (DSM) was developed to describe the dynamics of flexible polymer melts. The model is able to predict linear viscoelasticity of monodisperse linear, polydisperse linear and branched systems. The model also shows good agreement with dielectric relaxation experiments.

In this work both shear and elongational flow predictions obtained using the DSM are shown. Model predictions for shear flow agree very well with experimental results. The DSM is able to capture the transient response as well as the steady state viscosity. However, for elongational flow, agreement is unsatisfactory at large strains. The DSM captures onset of strain hardening, but after hencky strain of approximately 2, it predicts strain softening whereas experiments do not. We explore a number of assumptions of the model and their effect on flow predictions, including: finite extensibility, convective constraint release and activation of dangling ends. Only after careful examination of all approximations and assumptions can we conclude with certainty whether the standard view of entanglement dynamics is incomplete.

Thursday 10:50 Founders Ballroom B MB41

Crystallization and modelling of two different types of high-density polyethylene

Maziar Derakhshandeh and Savvas Hatzikiriakos
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The aim of this work is to study the effects of shearing, uniaxial extension, and temperature on the flow induced crystallization of two different type of high density polyethylene (a metallocene HDPE and Ziegler-Natta HDPE) using conventional rheometry. Furthermore, a model based on the suspension theory is proposed to predict the crystallization behaviour. Generally, extensional flow is found to be a stronger stimulus for polymer crystallization in comparison with shear causing crystallization at temperatures well above the melting peak point. The kinetic enhancement is found to be more dominant for the m-HDPE compared to the ZN-HDPE. The suspension model is found to predict the behavior at low deformation rates well, with deviations at higher rates in both shear and extension.

Thursday 11:15 Founders Ballroom B MB42

Toward tractable forms of ultra-high molecular weight polyethylene (UHMWPE)

Artemis Ailianou[1], Julia A. Kornfield[1], Giuseppe Forte[2], Sara Ronca[2], and Sanjay Rastogi[2]
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Ultra High Molecular Weight Polyethylene (UHMWPE) is remarkable: it has lower friction than polished steel, superior abrasion resistance, strength approaching that of steel and impact toughness even at low temperatures. The range of applications of the material is limited by the cost and difficulty of processing polyethylene with molar mass in excess of two million g/mol. Homogeneous catalysts can be used to produce UHMWPE that, in its nascent state, is amenable to melt drawing and other forming operations. Recent studies have introduced the concept of "unentangled crystals" to explain the dramatically different properties of the UHMWPE obtained immediately after polymerization by a homogeneous catalyst. To enable further investigation and use of this nascent form of UHMWPE, we present a simple method to reduce their agglomeration during polymerization. In our approach, we introduce an inert polymeric dispersant in solution with the homogeneous, single-site catalyst prior to introducing ethylene; we present evidence that polymerization of ethylene assembles a polymer brush as incipient nanoparticles form during polymerization and produces a stable, white colloid. We have shown that this colloid is easily mixed with polyethylene solutions to homogeneously disperse small concentrations of UHMWPE; these exceptional bimodal blends are of interest due to the dual effects of the UHMW chains on melt rheology and flow-induced crystallization. Hence, we focus on the nanoparticles in the "nascent" powders; using calorimetry, electron microscopy and synchrotron scattering we show that: (i) the first melting in DSC shows high melting UHMWPE that is intimately connected with the copolymer; (ii) SEM images reveal dramatic changes in nanostructure in the presence of the additive; and (iii) SAXS shows that the formation of the brush layer depends on the concentration of copolymer. Finally, we will present a conceptual model for the formation of colloids during polymerization.

Thursday 11:40 Founders Ballroom B MB43

Effective value of the dynamic dilution exponent in bidisperse linear polymers: From 1 to 4/3

Evelyne van Ruymbeke[1] and Hiroshi Watanabe[2]

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We revisit previously published dielectric and viscoelastic data of binary blends of linear cis-polyisoprene [Watanabe, H.; Ishida, S.; Matsumiya, Y.; Inoue, T. Macromolecules 2004, 37, 6619.] in order to test the validity of the Dynamic Tube Dilution (DTD) picture and to determine the most appropriate value of the dilution exponent α. We conclude that the DTD picture with $\alpha = 1$ is more appropriate at short times, while at longer time, a larger exponent of $\alpha = 4/3$ gives better description of the experiments. Furthermore, between these two time-regions, a broad crossover zone is found, going from an effective $\alpha = 1$ to an effective $\alpha = 4/3$. Based on this result, we propose to consider a new relaxation process, which is combined with the classical DTD picture with $\alpha = 1$ to give the effective $\alpha = 4/3$ at long times. This extra relaxation process results from the tension equilibration along the long chains, which takes place thanks to the blinking feature of release/reformation of the long-short entanglements. We quantify the relaxation function considering this tension equilibration and demonstrate its validity for description of the experiments in the entire range of time.

Thursday 12:05 Founders Ballroom B MB44

The role of nanoclay on the droplet deformation of PP/PET nanocomposite during the elongational field

Roozbeh Hajiraissi

Polymer Engineering, Islamic Azad University, Tehran, Iran

The aim of this research is to investigate the effect of elongation on the droplet deformation of the minor phase. The fiber spinning process induces fibrillar morphology. Therefore, the point-like structure has different characteristics in comparison with the fibrillar structure. Nanocomposite samples were prepared with constant weight ratio of matrix/disperse (PP/PET)(80/20), but varying in clay content (2%, 4%, and 6%). Maleic anhydride grafted Polypropylene PP-MA was used as compatibilizer to appraise its effect on morphology. To prepare samples, melt blending of the ingredients was performed in a twin-screw extruder. To obtain the fibrillar morphology, after melt blending, the samples were melt spun with a single-screw extruder equipped with spinneret. Characterization was performed with X-Ray diffraction (XRD) to study the morphology of nanoclay; melt visco-elasticity was determined via frequency sweeps and time dependence measurements of the dynamic visco-elastic properties. Also, scanning electron microscopy (SEM) was employed to observe the formed morphologies throughout the matrix. To evaluate the distribution of nanoclay, transmission electron microscopy (TEM) was employed. Results showed that increasing the amount of nanoclay hinders the fibrillation process and that compatiblizer serves as a negative factor against the extension of droplet during spinning.

Symposium SA

Self-Assembling, Associative and Gel-like Systems

Organizers: Suzanne Fielding and Andrew Belmonte

Thursday 8:40 Room 204 SA19

Modeling of the fingering instability in a reactive system

Andong He and Andrew Belmonte

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Beyond the classical viscous fingering for Hele-Shaw flows, anomalous fingering instabilities could occur as a result of chemical reaction on the interface. We examine the case when a gel-like substance is produced when two specially chosen Newtonian fluids meet in a Hele-Shaw cell. This reaction brings about significant changes in the interfacial tension, which is crucial in determining the stability of such a system. We model this by treating the interface as an elastic membrane whose bending stiffness depends on the local curvature. A dispersion relation is derived from the energy variation. We also classify several types of instabilities and determine the parameter regions where different instability occurs.

Thursday 9:05 Room 204 SA20

Association and dissociation rates in a simulated telechelic polymer gel

Mark Wilson[1], Arlette R. Baljon[1], and Avinoam Rabinovitch[2]
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The end-groups of telechelic associating polymers form aggregates that over time break and reform. At low temperatures, the number of bonds, F, between end-groups increases. The system undergoes a gel transition when $\partial^2F/\partial T^2=0$. In the gel the aggregate size distribution shows a distinct peak, whereas it decreases monotonically in the sol state. We will report how these changes in the aggregate size distribution are related to the kinetics of bond formation and breaking. To this end we simulate the system using a novel hybrid Molecular Dynamics (MD)/ Monte Carlo (MC) algorithm. The bead-spring model is used to update the position of the polymers in space using MD steps, while the bonds between end-groups form and break according to MC rules. In order to describe the aggregation process, we employ a master equation, defining the change in the number of aggregates of a certain size in terms of reaction rates. Those reaction rates depend on the sizes of the two aggregates that combine to form a large one or on that of the two aggregates into which a large aggregate splits. The reaction rates are obtained from the simulations for a range of temperatures. Using the measured rates, solutions to the master equation are shown to be stable and in agreement with the aggregate size distribution, as obtained directly from simulation data. Moreover, when limiting the master equation to single end-group attachment and release, the correct aggregate size distribution is obtained as well. In the model the micelle transition occurs at T=0.5, while a shoulder in the aggregate size distribution first appears at T=0.6 - the "onset temperature". We confirm that below the onset temperature deviations from Arrhenius behavior within relaxation times do occur. Furthermore, we show how variations in the reaction rates characterize the micelle transition near T=0.5.

Thursday 9:30 Room 204 SA21

Microscopic differences between shear bands obtained from simulations of associating polymers

Joris Billen and Arlette R. Baljon
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A hybrid molecular dynamics/Monte Carlo computer simulation is employed to study shear-banding in a simulation of temporary cross-linked telechelic polymers. Like in experimental studies at low temperature and/or high concentration, the system resists deformation. Upon application of a uniform shear at a rate slightly larger than the inverse relaxation time, the system yields. Subsequently, two distinct shear bands form. In this regime the stress is more or less independent of the applied shear rate. The differences in microstructure between the sheared and un-sheared system will be reported. So will those between the two shear bands. The concentration of monomers and associating groups in these two is the same. A major difference lies in the topologies of the respective networks, formed when end groups aggregate. For instance the sheared system contains more very large and very small aggregates than the un-sheared one. Even though the number of loops - chains that connect with both ends to the same aggregate- is not influenced by shear, the number of chains that bridge between the same aggregates increases. This effectively decreases the connectivity of the gel network, hence less connections have to be broken in order to shear it. Other differences, such as those in the lifetimes of the aggregates, will be reported as well.

Thursday 10:25 Room 204 SA22

Microrheology and microstructure of flow induced structured phase in wormlike micellar solutions

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It has been shown that surfactants can form long flexible cylindrical micelles (wormlike micelles) with the presence of some additives (e.g organic and inorganic salts) and under certain types of flows. In particular, cationic surfactants such as cetyltrimethylammonium bromide (CTAB) and some salts such as sodium salicylate(NaSal) have exhibited very unique viscoelastic behavior. In the last decade many research has reported that with proper concentrations of surfactant CTAB and salt NaSal the system could undergo a shear thickening after the shear rate reaches a critical value, while accompanying an increase of the shear viscosity, which was related to a strongly entangled wormlike micelles. Such structure exhibits gel-like features. Vasudevan et.al in 2008 showed that CTAB/NaSal solutions can create a stable flow induced structured phase (FISP) when subjected to a combination of shear and extensional flows. The present work shows a systematic microrheological study of FISP in a wormlike micellar system consisting of CTAB/NaSal by varying three salt concentrations, under different flow conditions and temperatures ranges. We apply particle image tracking microrheological technique to obtain the basic rheological properties such as relaxation time (τ), plateau modulus (G'), and zero shear viscosity (η_0) of the FISP. Using microfluidics techniques we built micro-hexagonal pillar arrays with different micropillar gaps (5, 10 and 15 μm) to vary the shear and extensional rates in microchannels with fixed flow rates. In addition, we also investigate the rheological and microstructure parameters of FISP correlating the rheological parameters of the structured phase with the microstructure features such as the mesh size of FISP. We also compare the microstructure obtained from the microrheology with the TEM measurements of FISP.

Thursday 10:50 Room 204 SA23

Switching between drag reduction and enhanced heat transfer of a reversible photo-responsive micellar solution

Haifeng Shi[1], Hyuntaek Oh[2], Yeshayahu Talmon[3], David J. Hart[4], Sean M. Pattison[1], Tyler A. Russell[1], Jacob T. Huggins[1], Srinivasa Raghavan[2], and Jacques L. Zakin[1]
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Some cationic surfactant solutions have drag reduction (DR) capability, and can be utilized in recirculation systems, like district cooling systems, to save pumping energy. But the heat transfer (HT) of DR solutions is also reduced in heat exchangers. Therefore it is of practical importance to enhance HT ability of DR solutions in heat exchangers while maintaining the DR in the rest of the circulation system. Switching between DR and enhanced HT of a photo-sensitive solution by light irradiation was studied in a solution of 5mM Erucylbis(hydroxyethyl)methylammonium chloride (EHAC) and 3.5mM sodium salt of 4-(phenylazo)-(E)-benzoic acid (PAB). The shear viscosity (eta) and first normal stress difference (N1) of this solution were measured before and after irradiation first with Ultraviolet (UV) and then visible light. The fresh solution showed Newtonian behavior with zero N1, and eta of 1.3cP. After UV irradiation the solution showed shear thinning and viscoelastic behavior. Eta decreased from 330cP at 0.1s-1 to 3.8cP at 1000s-1 and N1 increased from 0Pa at 0.1s-1 to 225Pa at 1000s-1. The UV irradiated solution also showed maximum DR of 29% in a rotating disk apparatus, while the fresh solution was not DR. The UV induced DR was lost after irradiation with visible light resulting in water-like behavior and enhanced HT. The changes in eta and N1, DR and HT were induced by changes in the nanostructure of the solution. Threadlike micelles (TLMs) were observed by cryogenic transmission electron microscopy in viscoelastic samples. UV irradiation changed the configuration of the N-N double bond of PAB, which promoted assembly of TLMs. Visible light reversed this process. The effects of UV and visible light on the configuration of the N-N double bond were demonstrated by UV-Vis spectra. The rheological changes of this photo-responsive surfactant system were reversible; recovering viscoelasticity after three cycles of alternate irradiation with UV and visible light.

Thursday 11:15 Room 204 SA24

Converging/diverging flow of wormlike micellar solutions

Michael Cromer[1], L. Pamela Cook[1], and Gareth H. McKinley[2]
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The pressure-driven flow of the VCM constitutive model (Vasquez, McKinley and Cook (2007)) through a planar channel of varying height is examined using a domain perturbation analysis. The shear-banded base state that develops in a 1D planar (straight-walled) channel is perturbed by a sinusoidal variation in the wall location, and the resulting linear system of partial differential equations governing the first order correction to the velocity and stress profiles is solved numerically. An overlapping domain-decomposition spectral method is developed to handle the sharp interfacial layer that arises as a result of shear banding. The two-species model predictions are compared and contrasted with the corresponding predictions of several single-species models, (e.g. the Oldroyd-B, PEC and Giesekus models) with a special focus on the converging regions of the periodic flow geometry. The computational results are also compared with experimental observations of the flow of wormlike micellar solutions through a microfluidic-based hyperbolic contraction/expansion geometry.

Thursday 11:40 Room 204 SA25

Structure, rheology and optical properties of plasmonic gels

Tao Cong, Satvik Wani, and Radhakrishna Sureshkumar
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We show that self-assembly of metallic nanoparticles (NPs) with wormlike micelles in solution is a robust route for producing stable multicomponent nanogels with exceptional color uniformity. Specifically, Au and/or Ag nanoparticles (NPs) of different size and shapes, in varying concentrations, are incorporated into a micelle network to obtain gels with localized as well as broadband optical absorption properties. Small angle X-ray scattering studies suggest that the NPs bridge micelle fragments to form a more compact double network. Such micelle-NP complexes exhibit intriguing rheological behavior which depends on the nanoparticle concentration as well as the salt/surfactant ratio. At relatively low NP concentrations, shear thickening behavior is observed indicating the formation of shear-induced structures. At intermediate NP concentrations, the gels are rheopectic over a wide shear rate range. At high NP concentrations, the viscosity of the gel decreases through three distinct shear thinning regimes. The mechanisms contributing to the rich rheological and optical properties of the plasmonic nanogels as well as their potential applications to solar energy harvesting and reconfigurable optical devices will be discussed.

Thursday 12:05 Room 204 SA26

The molecular origin of stress generation in wormlime micelles, using a rheo-SANS LAOS approach

Simon Rogers[1], Pavlik Lettinga[1], and Joachim Kohlbrecher[2]

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We combine large-amplitude oscillatory shear (LAOS) and time-resolved small angle neutron scattering (t -SANS) measurements on a dispersion of surfactant wormlike micelles. By viewing the responses as being the results of a sequence of physical processes, we observe new features of the system. We identify four distinct frequency regimes including a high frequency Maxwell-like, a yielding, a van der Waals, and a stable flow regime. For each regime we identify the molecular origins, on a Kuhn segment scale, of the stress response. We show the ability of the material to 'overorient' pre-yielding, compared to stationary shear banded flow. Finally, we present a stress-orientation rule which is rate-based at low frequencies and strain-based at high frequencies.

Poster Session

Symposium PO

Poster Session

Organizers: Suraj Deshmukh and Xue Chen

Wednesday 5:30 Founders Ballroom PO1

Panta rhei

Antony N. Beris[1] and A. Jeffrey Giacomin[2]
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This aphorism, "πάντα ῥεῖ," selected as the motto of The Society of Rheology (or "Τὰ πάντα ῥεῖ" for the Hellenic Society of Rheology), is attributed to one of the greatest of the Greek Ionian Philosophers, Heraclitus, ca 540-480 BC. However, a more careful investigation on the actual source of this aphorism, reveals that the first time it has been reported is much later than Heraclitus time, by the Roman Simplicius, ca 490-560 AD, as a comment rather than as a direct quote. It aims to concisely describe the central philosophical position of "becoming" or "change" in the form of a metaphor of "flowing" or "streaming" and as such we believe that it was and still is an excellent choice as a motto. In this presentation, we expand on its meaning, trace down other related quotes by Heraclitus and its followers, and explain its proper writing. We also trace down its history in The Society of Rheology and comment on various proposals for its possible change or improvement.

Wednesday 5:30 Founders Ballroom PO2

Examining the shear thickening behavior of chemical mechanical polishing slurries using high shear rheology

Nathan C. Crawford[1], Matthew W. Liberatore[1], S. Kim R. Williams[2], and David Boldridge[3]
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Chemical mechanical polishing (CMP) is a fundamental technology used in the semiconductor manufacturing industry to polish and planarize a wide range of materials for the fabrication of microelectronic devices (i.e., computer chips). During the high shear (=10^6 s^{-1}) polishing process, it is hypothesized that individual slurry particles begin to interact and collide with one another forming large agglomerates (>0.5 µm). These agglomerates tend to dig into the material surface causing defects such as scratches or gouges during polishing, which cost the semiconductor industry billions of dollars in lost production annually.

The slurries of interest consist of fumed silica suspended in water with added KOH for pH adjustment. Slurry contaminants, such as dust and oil, introduced during processing steps (i.e., pumping, mixing, filtration, etc.) are believed to heighten the agglomeration response displayed during polishing. Current thinking believes these agglomerates cause the slurry to shear thicken at shear rates relative to the CMP process. Our goal is to correlate shear thickening of the CMP slurry to the formation of agglomerates and to examine how the addition of various organic solvents and electrolytes influence the rheological behavior of the slurry.

Wednesday 5:30 Founders Ballroom PO3

Normal stresses in concentrated non-colloidal suspensions: Experiments and simulations

Talib Dbouk, Elisabeth Lemaire, Laurent Lobry, and François Peters
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We present an Experimental setup where suspensions of non-brownian mono-dispersed PMMA particles are sheared twixt two parallel disks inside a rheometer. Normal stresses are observed and easured upon shearing at different particles concentrations via some high precision pressure transducers that were installed in the setup. Different grid-holes were also made in the stationary disk which allowed us to measure the fluid pressure inside the suspension while shearing. The simultaneous measurements of shear stresses, normal stresses, and fluid pressure are presented. We adopted "the suspension balance model" first proposed by Nott and Brady (1994), and Morris and Boulay (1999), that describes the suspensions behaviour during the flow, and quantify the phenomenon of particles migration. We updated this model into two new versions. The first version includes the update of the original model according to our latest experimental data, where it quantifies well the concentration profiles of sheared suspensions, but it is limited to rheometric flows cases. In the second version the model was changed, such that the stresses in the suspension were correlated to its MicroStructure evolution, where general flows and the problems of relaxations that may occur at flows reversal can be taken into account. The conservative Finite Volume Method was used for the numerical discretisation of the PDE equations. Many suspensions flows inside numerous geometries were simulated, and the numerical profiles are compared to the experimentally measured ones.

Wednesday 5:30 Founders Ballroom PO4

Photogelation kinetics in Laponite-based colloidal fluids

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There has been significant interest in photoactive systems for a variety of potential applications. Recent work has opened the door to easily accessible photorheological (PR) fluids based on colloidal systems. However, there is very little work on the kinetics of gelation of such PR fluids. We present a detailed study on the kinetics of photogelation of a simple photoactive system based on a dispersion of Laponite nanoparticles with a surfactant and photoacid generator (PAG). The kinetics of gelation were probed using in-situ photorheometry. These samples were further characterized using differential scanning calorimetry (DSC) and dynamic light scattering (DLS) as well as ex-situ monitoring of pH evolution as a function of UV and thermal exposure. The experiments focused on identifying the factors influencing the gelation by monitoring the evolution of viscosity as a function of time under different conditions. We demonstrate the effect of composition and gelation conditions on the kinetics of gelation and also show how the final gel properties can be tuned. Finally, using these results, we propose a generalized scheme for the design of these active dispersions.

Wednesday 5:30 Founders Ballroom PO5

A rapid, inexpensive technique for measuring the rheological properties of yield stress fluids

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Yield stress fluids like emulsions, foams, composites and fiber suspensions are present in many different industries. The yield stress is the most important rheological parameter for the design of industrial processes and equipment. There are numerous methods for measuring yield stresses, ranging from simple practical methods to techniques employing sophisticated rheometers. The most appropriate method can vary from one material to another as well as from one application to another.

Interest in the rheology of lignocellulosic biomass has increased with the development of processes to convert this material into chemicals such as liquid fuels. Yield stress measurements for biomass suffer from a number of instrument and material related difficulties including wall slip, sample ejection, stresses exceeding sensor capacity and sample separation into multiple phases. Measurements are often made using a vane geometry, but this approach is limited to low solids concentrations. Torque rheometry can be used at higher solids concentrations, but this technique can be quite slow (approximately 1.5 hr for a single measurement). Both apparatuses are expensive, with costs in the range of $50,000-$100,000.

We will describe an inexpensive, rapid method for measuring the rheological properties of yield stress fluids which avoids many of the material and instrument difficulties mentioned above. The method can be used on all yield stress fluids including those with very large yield stresses such as those found in highly concentrated biomass. The technique employs a direct measure of yield stress, in that extrapolation of shear stress data to zero shear rate is not required. Measurements do not alter or disturb the sample prior to measurement, which can be a significant issue in conventional methods. We will show that measurements using this technique compare well with measurements obtained using conventional equipment and methods.

Wednesday 5:30 Founders Ballroom PO6

Suspension rheology of polymer particles with thermosensitive deformability

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The rheology of particulate suspensions has been observed to be a strong function of particle deformability. For example, the shear thinning of red blood cell suspensions is shown to increase with an increase in the deformability of the cell membrane, with important implications for circulatory behavior [Magnus I. Gregersen, Science (1967)]. Likewise, shear thickening is nearly ubiquitous in concentrated suspensions of rigid particles but almost absent in suspensions of softer, more deformable objects [Howard A. Barnes, Colloids and Surfaces (1994)]. However, we still lack a comprehensive description of the role of particle deformability in suspension rheology. This is due in large part to the difficulty of systematically and independently varying particle rigidity, volume fraction, interaction strength and size. We report here on the synthesis and characterization of a colloidal system that permits such variation. Sterically stabilized non-crosslinked particles are produced by emulsion polymerization in the presence of a reactive surfactant. The use of a reactive species allows the surfactant to be covalently attached to the particle, with the degree of stabilization tunable by the molecular weight, concentration and species of the surfactant. The glass transition temperature of the polymer is close to room temperature and so given the absence of cross-linking, the elasticity of the particles can be changed over several decades simply by manipulating temperature in an experimentally convenient regime. For a fixed time-scale, below Tg, particles behave as near-rigid spheres, while, above Tg, they are soft yet viscous droplets with structural flexibility. We present results of dilute and concentrated suspension rheology for a series of particle sizes and interaction strengths. We tentatively interpret our data based on the relative magnitude of the polymer relaxation time and the rheologically defined timescale.

Wednesday 5:30 Founders Ballroom PO7

Large amplitude oscillatory shear analysis of electrorheological fluids structures

Aadil Elmoumni and Aloyse Franck
TA Instruments, New Castle, DE 19720, United States

Electro rheological (ER) fluids are suspensions of extremely fine non-conducting particles in an electrically insulating fluid, which show dramatic and reversible rheological changes when the electric field is applied. These changes in apparent viscosity can be up to five decades in magnitude and the suspensions can go from the consistency of a liquid to that of a solid, and back, with response times on the order of milliseconds. Large amplitude oscillatory shear experiments were conducted to probe the changes in the non-linear viscoelastic properties of an ER fluid with respect to the voltage applied. Changes in the material structure are characterized as a function of the applied voltage and strain amplitude using non-linear parameters such as minimum and large amplitude modulus G'_M and G'_L. Effect of voltage on intra-cycle stiffening and test frequency are analysed.

Wednesday 5:30 Founders Ballroom PO8

Activated nanocage-polymer electrorheological fluids

Ernest C. McIntyre
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We show that mixtures of small amounts (~1%) of sulfonated polyhedral silsesquioxane (s-POSS) nanocage with polystyrene (PS) microspheres and poly dimethyl siloxane (PDMS), exhibit significant electrorheological activity; the magnitude of the effect is comparable to that of conventional polymer ER systems. While the s-POSS/PDMS system is weekly ER active, the magnitude of the ER effect in the s-POSS/PS/PDMS mixture is more than an order of magnitude larger. The enhancement appears to be related to an interfacial interaction between the PS spheres and the s-POSS molecules, which possess permanent dipole moments. This effect is strongly dependent of nano-sphere size.

Wednesday 5:30 Founders Ballroom PO9

Preparation of monodisperse silicon nanocrystals through density-gradient ultracentrifugation in organic solvents

Joseph M. Miller[1], Austin R. Van Sickle[1], Ganjigunte Iyer[1], Rebecca A. Anthony[2], Uwe R. Kortshagen[2], and Erik K. Hobbie[1]
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Monodisperse colloidal suspensions of ligand-stabilized silicon nanocrystals, synthesized through a nonthermal low-pressure plasma reaction, are prepared through density-gradient ultracentrifugation in organic solvents. Density-gradient profiles of mixed chloroform and m-xylene are used to control the settling speed of the colloidal nanoparticles and hence optimize their transient separation by size along the depth of polyoxymethylene ultracentrifuge tubes. The mean size and polydispersity of the extracted fractions are characterized through photoluminescence spectroscopy and transmission electron microscopy, and the self-assembly of fractions into amorphous solids and close-packed crystal lattices is achieved using an immiscible two-fluid evaporation scheme. The photophysical properties of the purified nanocrystal assemblies are compared with those of the starting materials, and the influence of atmospheric oxygen and temperature on the stability of nanocrystal ensemble photoluminescence is measured. We also measure the mechanical stability of nanocrystal monolayers that have been self-assembled on soft polymer substrates and over submicrometer holes in TEM grids.

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Wednesday 5:30 Founders Ballroom PO10

Clustering and gelation of attractive colloidal suspensions in confinement

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Colloidal suspensions flowed in confined geometries, such as nozzles, microchannels, thin films, or porous materials, are frequently encountered in industrial and technological settings, ranging from drilling mud for geotechnical engineering to inks for printing and direct-write assembly. For hard sphere suspensions, confinement has been previously shown to affect both the crystallization and vitrification of colloidal suspensions, causing both to occur at lower volume fractions than in bulk. Here, we use confocal microscopy to elucidate the effect of confinement on the structure and phase behavior of attractive colloidal suspensions. We find that in colloid-polymer depletion mixtures flowed into wedge-shaped chambers, gelation occurs at lower strengths of attraction in thin geometries than in bulk. At constant strength of attraction, increasingly confining the sample induces phase transitions. For relatively weak attraction, the sample changes from a fluid to a crystal to a gel with increasing confinement. For relatively strong attraction, the sample changes from a fluid to a fluid with clusters to a gel with increasing confinement. The average cluster size and percentage of particles contained within clusters increase across this fluid to gel transition. Concurrently, the particle dynamics show significant slowing and a transition to subdiffusive behavior. These results suggest that this apparent gelation transition in confined colloid-polymer mixtures arises due to a complicated interplay between suspension rheology and wall-induced structuring.

Wednesday 5:30 Founders Ballroom PO11

Development of a cement-based magneto-rheological fluid

Sriramya D. Nair and Raissa P. Ferron
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In this study, micron sized magnetic particles are added to cement paste to form a cement-based magneto-rheological (MR) fluid. In the presence of an external magnetic field, MR fluids experience rapid rheological changes. When an external magnetic field is applied, the magnetic particles align along the direction of magnetic filed and form chain like structures. These chains restrict motion of the fluid and thus there is an increase in the viscosity. Traditionally MR fluids are used in several applications, such as dampers, brakes and many more. Cement-based MR fluids can potentially be used in civil engineering applications to act as a "set on demand" material. If successful this will allow real-time control of the stiffening behavior of cement-based fluids. In this poster we show preliminary results showing the affect of different magnetic particle concentrations and different magnetic fields on the rheological properties of cement-based fluids.

Wednesday 5:30 Founders Ballroom PO12

Modeling fracture in polymeric fluids under step shear

Okpeafoh S. Agimelen and Peter D. Olmsted
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The Doi-Edwards tube model predicts a shear stress maximum as a function of the shear rate, at a shear rate roughly the reciprocal of the longest relaxation time. The consequence of this is instability which can lead to shear banding. Although different modifications have been made to the original theory due to the difficulty in seeing this stress maximum in early experiments, recent experiments have revealed the existence of shear banding in polymer solutions. Closely related to this is the phenomenon of stress overshoots during start-up of shear. Stress overshoot is characteristic of solids during yielding and this elastic character is contained in the Doi-Edwards tube model.

In a recent experiment, Pouyan et al. observed fracture in melts of styrene butadiene subjected to large shear/strains. However, they interpreted this to mean a total collapse of the entanglement network after an initial yielding; this would not be possible in the framework of the tube model. Hence it became necessary to check if this surprising phenomenon could be related to the idea of strain localization in polymers which is predicted by the original tube model. Strain localization is associated with yield-like behaviour, which leads to anomalous behaviour.

Results from our calculations show good qualitative agreement with experimental data. The build-up of a very narrow high shear rate layer in the material after shear cessation may be due to strain localization in the material. This narrow high shear rate layer ultimately leads to slip of the two outer layers and hence fracture. The results suggest fracture may be related to type C anomalous behaviour associated with stress relaxation in polymers under high enough strain and with sufficient number of entanglements.

Wednesday 5:30 Founders Ballroom PO13

Current and proposed rheological methods for characterizing asphalt binders

Gregory W. Kamykowski
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Rheological characterization is performed extensively in the asphalt industry. Several test methods that are unique to the asphalt industry have been developed, with the goal of predicting pavement resistance to failure modes such as rutting and cracking. These tests have consisted primarily of determining dynamic rheological properties of binders at a specified frequency and strain over a range of temperatures. These tests have become accepted and mandated by state Departments of Transportation. As asphalt binders have become more complex through blending, primarily with elastomers, and correlations with pavement performance have been refined, additional tests have been proposed and are being explored. Some are near acceptance by the industry, such as the Multiple Stress Creep and Recovery (MSCR) test. Others are in various stages of development. Examples of these are the Mixing and Compaction Test, wide-gap concentric cylinder testing, torsion cylindrical testing, and the Linear Amplitude Sweep Test. This poster will describe the rheological tests that have become accepted in the asphalt industry as well as the developing tests and will illustrate what is required from a rheometer and its software to run the instrument and perform data analysis.

Wednesday 5:30 Founders Ballroom PO14

In-situ monitoring technique for microstructural changes of cement paste via rheology

Dongyeop Han and Raissa P. Ferron
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The microstructural changes that occur during shearing of cement paste have a strong impact on the fresh state properties of concrete. However, due to the high opaque nature and high solid concentration of cementitious pastes, many studies aimed at microtrustrucal analysis during the fresh state often uses samples that are very dilute or altered by other techniques (e.g. cryogenic microscopy analysis). In this study, the microstructure of unaltered cement pastes was observed using an in-situ technique so that information about the microstructural changes that occurred during shearing could be obtained. To gain better insight about the rheological properties of cement paste, the role of solids concentration, type of chemical admixtures, and shearing conditions were examined . For the shearing conditions, higher shear rate breakdowns microstructure and the counts of smaller particle was increased by increasing shear rate. Higher concentrated sample has more flocculation forces and particle numbers were higher than lower concentrated samples while smaller particle was counted less. HRWR disperses cement particles well and accelerator aggregates particles more.

Wednesday 5:30 Founders Ballroom PO15

Correlations of mixture rheology with clay aggregate size and concentration for oil sands slurries

Jessie Smith and R. Sean Sanders
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Canada's oil sand reserves provide more than 1 million barrels of crude oil per day and much of the gasoline and diesel fuel used in western Canada comes from this source. In the mining of oil sand and extraction of bitumen, aqueous slurries containing bitumen, coarse sand and fine clays are produced. The performance of key process units (e.g. conditioning slurry pipelines, gravity separation vessels, mechanical flotation cells and hydrocyclones) is strongly dependent on the density and viscosity of the so-called "carrier fluid", which is comprised of the fine (< 44 μm) solids and the water. The viscosity depends on numerous factors including fine solids concentration, particle mineralogy and water chemistry. Despite the importance of this parameter in process design and monitoring, it is rarely measured.

In the current study industrial samples of tailings and oil sands hydrotransport materials were examined. The primary objective was to correlate the rheological behavior of the carrier fluid with aggregate size and concentration, thereby allowing operators to use particle size analysis to infer carrier fluid viscosity. Slurry samples were separated into their coarse and fine components. The carrier fluid was then tested in a rheometer and aggregate size and concentration determined using a flow particle image analyzer (FPIA). Preliminary results indicate that reliable viscosity predictions can be obtained from measurement of the aggregate size and concentration in these industrial slurries.

Wednesday 5:30 Founders Ballroom PO16

A rheo-chemical study of vinyl ester-clay systems

Jia Liu, Hatsuo Ishida, and João Maia
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A Rheo-chemical Study of Vinyl Ester-Clay Systems Jia Liu, Hatsuo Ishida, Joao Maia Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, 44106, USA Abstract Nanocomposites of Vinyl Ester (VE) with 48 wt.% styrene content (ST) were prepared by melt in-situ polymerization with different loadings of organically-modified montmorillinte clay (MMT) . The microstructure and morphology of the nanocomposites were examined by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). XRD and TEM results indicated that VER-Clay nanocomposites had predominantly exfoliated morphologies. The dynamic and steady shear rheological properties of the nanocomposites showed remarkable differences in comparison to that of pure VER-ST copolymer. The correlation between structural changes and rheological properties was evaluated by isothermal Fourier transforms infrared (FTIR) spectroscopy. The influence of shear on the exfoliation of VER-Clay nanocomposites has also been studied and will be discussed.

Wednesday 5:30 Founders Ballroom PO17

Linear algebra yielding in LAOS

Simon Rogers and Pavlik Lettinga
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The nonlinear yielding responses of three theoretical models, including the Bingham, a modified Bingham, and Giesekus models, to large-amplitude oscillatory shear (LAOS) are investigated under the framework proposed recently by Rogers et al [J. Rheol. 55(2), 435-458 (2011)]. Under this framework, basis states are allowed to wax and wane throughout an oscillation, an approach that conflicts directly with the assumptions of all Fourier-like linear algebraic approaches. Full yielding descriptions of the nonlinear waveforms are attained by viewing the responses as representing sequences of physical processes. These interpretations are compared to, and contrasted with, results obtained from linear algebraic analysis methods: Fourier-transform rheology [Wilhelm, M. Macromol. Mater. Eng., 287, 83-105, (2002)]; and the Chebyshev description [Ewoldt et al J. Rheol. 52(6), 1427 - 1458 (2008)] of the so-called elastic and viscous stress components sigma' and sigma" [Cho et al J. Rheol. 54(1), 27 - 63 (2010)]. Further, we show that the discrepancies between the built-in model responses and parameters, and the interpretations of the Chebyshev and Fourier coefficients are directly related to misinterpretations of sigma' and sigma" as being the elastic and viscous stress contributions. We extend these ideas and discuss how every linear algebraic analysis is incapable of producing physically meaningful information when a material yields.

Wednesday 5:30 Founders Ballroom PO18

Evaluation of rheological behavior of water and oil based drilling mud in gas hydrate formation: Preliminary results

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Gas hydrates are solid structures formed by hydrogen bond between water molecules that trap low weight gas molecules or light hydrocarbons at low temperatures and high pressures. Despite being a great resource on energy for oil and gas industries, hydrates are a big problem because they can clog pipelines, Christmas tree valves and wellhead affecting oil and gas distribution. In drilling operations, problems caused by hydrate formation include choke and kill line and wellbore plugging below the BOP, plug formed around the string inside casing and riser, preventing drill pipe trip, and so on. Furthermore, gas liberation near surface during hydrate decomposition may create a dangerous well-control situation besides that the amount of water needed for crystal formation could come out from the drilling mud, changing its flow properties as well. The gas enters the drilling fluid and changes its rheological behavior, viscosity, weight, etc. Different methods can be used to detect the moment of hydrate formation. Differential scanning calorimeter and rheometer are examples. Herein, we used a rheometer to evaluate the rheological behavior of drilling mud through a gas hydrate bearing formation. Tests were performed with water and oil based drilling mud by using a concentric-cylinder rheometer pressurized at 4500 psi with methane and nitrogen. A temperature sweep method was used in order to determine the peak in the viscosity curve, characterizing a hydrate formation for both drilling fluids at different concentrations. A factorial complete design, with two factors - temperature and mud concentration - and three central points was used.

Wednesday 5:30 Founders Ballroom PO19

Composite materials with viscoelastic stiffness greater than diamond due to a negative stiffness phase

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Negative stiffness can give rise to extreme physical properties such as stiffness, damping, thermal expansion, piezoelectricity, etc.,in heterogeneous systems. Negative stiffness is anticipated in ferroelastic materials such as BaTiO3 near the phase transformations. In this study, extreme anelastic responses (stiffness greater than diamond and large amplification of damping) have been observed in ZnAl-BaTiO3 composites near the tetragonal-orthorhombic transformation temperatures of BaTiO3. Weak responses near the Curie point is due to a large spontaneous strain of the inclusions.

Wednesday 5:30 Founders Ballroom PO20

Heterogeneity: A solution to the mysteries of the glass transition?

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For most phase transitions, dynamic slowing down is accompanied by static structure changes. However, for the supercooled liquid, which is a special liquid state in which crystallization below the melting temperature has been avoided, one finds a pronounced dynamic slowdown. Here, diffusion coefficient, relaxation time and viscosity change over 14 orders of magnitude within a relatively small temperature range, without any static structure change. Over the past several decades, extensive research has been performed in order to understand why the glass transition occurs? What the glass transition exactly is? And how molecules move near to the glass transition? In the present work, the idea that dramatic dynamic slowdown of a supercool liquid during cooling from above the Tg occurs because of the increasing length scale of heterogeneous subregions, or the Cooperative Rearrange Regions (CRR) proposed by Adam and Gibbs, is evaluated by analyzing experimental and computer simulation results related to material heterogeneity. Although the existence of microscopic heterogeneous regions is confirmed, the variabilty in the fitting parameters obtained from the VFT and power law fits of the temperature dependence of the heterogeneity data suggest that the heterogeneity might not play the key role in the Tg and/or tightly connect with the CRRs.

Wednesday 5:30 Founders Ballroom PO21

Shear thickening, shear thinning and obviation of yield stress in aluminum dispersions

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Recent rheological examination of the viscosity-shear stress profiles of five identically prepared, aluminum dispersions revealed two different behaviors. Three batches showed a shear thickening behavior of viscosity-shear stress profiles. Two batches, however, showed high yield stress values and shear thinning behavior at higher shear stress. This masking of the shear thinning regime with high shear stress values agrees well with data and conclusions described in E. Brown, et al., Nature Materials Letters, January, 31, 2010 (DOI: 10.1038/NMAT2627). This phenomenon will be related (where possible) to the colloid chemistry and processing of the aluminum dispersions involved.

Wednesday 5:30 Founders Ballroom PO22

Temporary bond-debond technology for flexible electronics: Impact of adhesive properties on performance

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For fabrication of flexible electronics using standard microelectronics toolsets, a temporary bond-debond method has been developed that requires minimization of the distortion of bonded flexible substrate and bow of bonded system (flexible substrate-adhesive-carrier) during processing. To elucidate the critical parameters of the adhesive used in the bonding that control the stress (bow) and distortion, adhesives with different viscoelastic properties are examined systematically. By blending a high modulus adhesive into a low modulus adhesive, the storage modulus, loss modulus and loss factor of adhesive can be tuned by orders of magnitude. Examining the impact of these three rheological parameters on the stress and distortion of bonded system, the relative viscoelastic flow property of the bonding adhesive to that of the bonded flexible substrate appears directly correlated to bow and distortion. When the loss factor of the adhesive is less than that for the plastic substrate, precise registration of layers during photolithography is observed. These results provide insight into the rheological parameters critical to the adhesive formulations for the temporary bond-debond method in the fabrication of flexible electronics.

Wednesday 5:30 Founders Ballroom PO23

Flow induced crystallization of a semiconducting polymer

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The crystallization of semiconducting polymers is critical to their performance in a photovoltaic device since this dictates their electrical transport properties, in particular the hole mobility for most systems. Many polymer-based solar cells are manufactured in the laboratory by spincoating requiring that a low viscosity liquid must be used to make a smooth film. This of course suggests the solution should have very little structure within it. Thus, crystals are made during the rapid spincoating process. However, industrial scale manufacture will use continuous production methods such as roll-to-roll or slot die coating. In this case it is not clear what rheological properties are required to make a solar cell nor whether the fluid should be structured prior to coating the substrate. Furthermore, during processing the solution may spend significant time under a deformational flow that could change its properties. We have sheared solutions of poly(3-hexylthiophene) in a non-volatile solvent to determine its flow induced crystallization behavior. Without shear the polymer crystallizes very slowly, however, during shear the crystallization rate can be significantly increased and the viscosity rapidly rises. This can have a significant influence on the coating properties. For example, if a solution is exposed to continuous shear while in the bath supplying material to a roll coater its properties could change during production and negatively influence the solar cell performance. Here we show the effect of shearing time and rate on the crystallites formed as well as the rheological properties during shear.

Wednesday 5:30 Founders Ballroom PO24

Experimental studies on the dynamics and stability in Anilox roll coating process

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The final goal of most coating flows is to produce uniform coating liquid layers of specified thickness at high speeds. The study on the dynamics and optimal coating windows in coating processes is quite important industrially as well as academically, because it is closely related to productivity and high quality control of coating products, especially, in films, flat panel displays, batteries, and steel products. Among many coating processes, in this study, Anilox roll coating processes have been experimentally investigated, which are distinguished by the use of one or more gaps between rotating rolls to meter and apply a liquid to web or substrate. To examine the flow dynamics of Newtonian and viscoelastic liquids near coating beads in both processes, coating thickness and positions of dynamic contact line or meniscus have been measured under various operating conditions, using the flow visualization apparatus. Also, coating windows of Newtonian and viscoelastic liquids in anilox roll coatings have been established, respectively. In the forward roll coating, the viscoelasticity aggravates the ribbing instability, meaning that ribbing occurs under the lower roll-speed conditions in viscoelatic case. The destabilizing effect of the viscoelasticity is caused by the high elastic stress near the downstream region, prominently making the pressure gradient in the downstream positive. There are two instability modes in the reverse roll coating: ribbing in low speed ratio of metering roll and applicator roll and cascade in high speed ratio between both rolls (In the middle speed ratio, stable region exists). It has been observed that in this system the viscoelasticity produces the stable regime at higher speed ratio than Newtonian case. This result may be also closely related to the extensional flow near the downstream metering flow region. We have concluded that extensional properties in coating liquids play a key role in determining the optimal coating windows and the coating performance.

Wednesday 5:30 Founders Ballroom PO25

Experimental studies on coating dynamics of various polymeric primer paints in 3-roll coating process

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Dynamics and instabilities of various polymeric primer paints for manufacturing automotive pre-painted metal sheets have been experimentally carried out using multiple 3-roll coating equipment. Considering the polymeric paints with shear-thinning rheological properties, their coating windows demarcating ribbing, stable, and cascade regions have been established by changing coating operations such as speed ratio, rotation direction of rolls, and positive/negative gaps. In the stable region obtained in reverse-mode roll coating, dry coating thickness increased with decreasing speed ratio and increasing metering gap. The severity and wavelength of ribbing instability which represents cross-web variation of coating thickness have been compared under different coating conditions.

Wednesday 5:30 Founders Ballroom PO26

Dilute solution coil dimensions of branched polymers in synthetic oils

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Polymer dilute solution properties have been studied in detail for polymer architectures such as linear, star, and comb structures. However, dilute solution studies on dendritic type architectures are sparse. Here we present dilute solution results on dendritic type polymers in poly-alpha-olefin solvents. Radii of gyration, hydrodynamic, and viscometric radii are measured as a function of temperature, and compared to linear and star polymers of the same chemical species.

Wednesday 5:30 Founders Ballroom PO27

Investigation of mechanical properties of polymer membranes for alkaline exchange fuel cells

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While proton exchange membrane (PEM) fuel cells have been the focus of development in the past, anion exchange membranes (AEM) have the potential to dramatically lower the cost of fuel cells by utilizing non-noble catalysts and a variety of fuel sources. As part of a broader effort to develop novel, cost effective AEMs, creating mechanically robust polymer films is important. Thus, performing mechanical characterization under fuel cell operating conditions, which requires the development of an environmental chamber to control a wide range of humidity at various temperatures, is needed. Preliminary work on synthesis, processing and the rheology of conducting polymer films as well as simulation work on environmental chamber design will be presented.

Wednesday 5:30 Founders Ballroom PO28

Evaluation of creaming and sedimentation for nutritional beverages via analytical centrifuge, particle size analysis and rheology

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In this poster, we evaluated the physical stabilities of emulsion based nutritional beverages using analytical photocentrifuge (LUMiSizer 610), laser diffraction particle size analyzer, and rheometer. Although Stokes law gives us a great insight into how fast an individual particle moves in dispersion, the complexity of nutritional emulsions with numerous ingredients that current market requires complicates stability analysis. As such, an analytical photocentrifuge was employed to visualize the progress of dispersion instability, and to calculate velocity distribution of fat globules, cream layer/supernatant interface velocity, thickness and firmness of sediment layers. We applied average centrifugal force between 530 to 2100g to accelerate dispersion instability/separation of infant formulas and medical/adult nutritional beverages with different proteins, minerals, stabilizers and emulsifiers. This photocentrifuge tracks the transmission percentage as a function of position across the sample cell height to examine various instability mechanisms. The operating software (SEPView 6.0) accurately illustrated the thickness of sediment layer; any significant changes in sediment layer thickness in response to increasing centrifugal force during run indicated how soft the sediment layer was. As compared to these tests, which do not depend on viscosity and particle size, screening formulations at zero time, and predicting the shelf life of screened candidates require some modifications to velocity measurement because viscosity of a complex emulsion, which directly affects creaming velocity, changes with centrifugal force. Particle size analysis first helped to calculate the shear rate that a particle actually "feels" in dispersion, and viscosity profile as a function of shear rate examines the viscosity difference between 1g and the applied centrifugal force. These results demonstrated a good correlation with the actual shelf life study.

Wednesday 5:30 Founders Ballroom PO29

Rheology on large particle suspensions from saccharification processes

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Understanding rheological behavior of large particle suspensions is of increasing importance for biomass-ethanol conversion. Biomass, i.e. corn stover or other cellulosic pulp, react in aqueous slurry by a saccharification reaction. During this reaction cellulosic material is broken down and thus the size of the particles decreases. Understanding rheological properties of these suspensions is important for process improvements, i.e. better mixing, pumping etc. Especially during startup yield stresses can occur, which pose potential problems. There are several obstacles to reproducible and meaningful rheological characterization of these materials. Particles are initially larger than the gap in the conventional shear geometries, which prevents data acquisition for the early stages of the saccharification reaction with these geometries. Suspensions settle over time, which makes rheological data irreproducible and very difficult to interpret. Our laboratory evaluated geometries for rheological characterization of highly loaded, unstable suspensions with particles much larger than the gap of conventional geometries. The viscosities of Brookfield silicone fluid viscosity standards and a shear thinning viscosity standard from NIST were measured using narrow gap concentric cylinder, vane, helical ribbon, and a Starch Pasting Cell. The bias of these geometries is compared to the conventional ones using the Newtonian and shear thinning standards. Both the vane and the helical ribbon appear to be good choices for measuring the viscosity of unstable suspensions containing large particles. With these tools rheological experiments were conducted on a series of samples taken at various reaction times from the above mentioned saccharification reaction and are briefly discussed.

Wednesday 5:30 Founders Ballroom PO30

How to obtain a galactomannan standard for solution rheology?

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Water-soluble polysaccharides extracted from legume seed endosperms such as galactomannans and are well known as viscosifiers due to their high molecular weight. The molecular structure has been found to consist of a backbone of mannose with galactose sidegroups at variable degree of substitution according to the specific plant source [1-2]. Galactomannan polysaccharides extracted from seed endosperms of various species have been characterized by size-exclusion chromatography, dilute-solution viscometry, and oscillatory-shear rheology to determine their potential as aqueous thickeners. The molecular composition and chain-length distribution were found to be nearly identical, and thus

galactomannans within the same genus are presumed to share a common molecular structure. Obtained scaling properties suggest that in contrast to common belief, water can be considered as a good solvent and therefore the Colby-Rubenstein model can be utilize to describe galactomannan solution rheology [3]. Solutions above the crossover concentration exhibited shear-thinning behavior, and strong dependence of viscosity on concentration. Seed characteristics such as shape, mass, and endosperm content were also assessed, and based on this investigation, some legume endosperms are advantageous for industrial processing and could be adapted for e.g. guar gum replacement [4-6].

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Wednesday 5:30 Founders Ballroom PO31

Dilatation rheology of protein fibers at fluid-fluid interfaces

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The mechanical stabilization of a liquid-liquid interface using protein fibers of is investigated experimentally. Protein fibers are obtained by combined pH and heat denaturation of globular food proteins. These fibers bear many similarities with amyloid fibers, but can be tuned in their shape, flexibility, length and charge density by using various production protocols [1]. To address the rheological properties of these fibers at the liquid-liquid interface we use interfacial shear and dilatational rheometry probing directly the transient evolution of the mechanical properties [2]. The protein fiber aggregation at the interfaces is ruled by both, adsorption and denaturing steps, which eventually lead to a dense adsorption layer. Dilatational rheometry show that depending on the adsorption kinetics and experimental time, parameters such as dilational viscosity and elasticity are corrupted by superimposed protein adsorption. A proposition is made to account for the time scales during protein adsorption and mechanical deformation.

1. Jung JM, Gunes DZ, Mezzenga R: Langmuir 26 (2010) 15366-15375; 2. Erni P, Windhab EJ, Fischer P: Macromol. Mater. Eng. 296 (2011) 249-262.

Wednesday 5:30 Founders Ballroom PO32

Stick-slip motion of the contact line of water droplets coated with insoluble surfactants

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The motion of a sessile droplet of water moving on a smooth horizontal substrate can be described by the Cox-Voinov model, linearly relating the cube of the contact angle to the speed of the contact line and the inverse of the surface tension. This surface tension can be modified by depositing a layer of surface-active species at the air-water interface, e.g. colloidal particles or amphiphilic molecules such as surfactants. Insoluble surfactants in particular can exhibit a variety of interfacial visco-elastic behaviors, ranging from Newtonian to highly elastic. In previous experiments conducted by Leiske et al., for droplets covered with different elastic layers, such as dipalmitoylphosphatidylcoline (DPPC) and Meibum - a lipid layer secreted to stabilize the tear film covering the cornea of mammals -, a stick-slip motion of the contact line was recorded at low moving velocities [1]. Using a similar apparatus, we investigate further this stick-slip phenomenon by studying the influence of the different experimental parameters.

[1] Influence of surface rheology on dynamic wetting of droplets coated with insoluble surfactants. Danielle L. Leiske, Cécile Monteux, Michelle Senchyna, Howard A. Ketelson and Gerald G. Fuller, **Soft Matter**, 2011, Advance Article.

Wednesday 5:30 Founders Ballroom PO33

Collective behavior of active particles in an Oldroyd-B suspending fluid

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The literature is rich with the studies of the individual and collective behavior of active particles in Newtonian suspending fluids. However, many biological fluids like mucus and saliva exhibit viscoelasticity. Although many works have investigated the effects of viscoelasticity on a single organism, no work exists on the impact on the collective response. We have analyzed the collective behavior of active particles in an Oldroyd-B suspending fluid. In addition to being well a studied viscoelastic constitutive equation, the Oldroyd-B fluid corresponds to a polymer solution like saliva. Following previous works, we have quantified the collective behavior of bacteria by a linear stability analysis of the uniform isotropic state using a mean field theory. We have compared the results with the case of Newtonian fluid to understand the influence of viscoelasticity. We have observed that, in contrast with the Newtonian result, the most unstable collective structure may be located at intermediate wave lengths depending on Deborah number and the polymer contribution to viscosity.

Wednesday 5:30 Founders Ballroom PO34

Rheology of photocrosslinkable alginate hydrogels with encapsulated mesenchymal stem cells

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Photocrosslinkable hydrogels are useful biomaterials for tissue engineering scaffolds as they can be formed *in situ* under conditions that maintain the viability of encapsulated cells. Rheology is commonly used to characterize such hydrogels because their mechanical properties will affect their performance as biomaterials. However, this characterization is usually done on fully crosslinked hydrogels without cells, while in practice the presence of cells may influence the constructs' gelation rate and material properties. In this work, methacrylated alginate, with and without coupled cell adhesion ligands, was used as a biomaterial to study how encapsulated cells affect the hydrogel crosslinking kinetics and mechanics. A rheometer with a UV photocuring bottom plate fixture was used to measure changes in hydrogel modulus during photocrosslinking *in situ*. Real-time crosslinking studies using this system demonstrated that the presence of covalently coupled peptides containing a cell adhesion ligand (arginine-glycine-aspartic acid or RGD) did not significantly affect the gel point or plateau modulus in these hydrogels at the cell and peptide concentrations examined. The addition of human mesenchymal stem cells, a cell population commonly used in tissue engineering, at concentrations of 1-5x10^6 cells/ml resulted in a trend of decreased plateau modulus compared to hydrogels without cells. The effect of encapsulated cells on crosslinking kinetics was also examined. Further investigations are ongoing examining the influence of different cell types and concentrations on these UV crosslinking parameters to gain insight for future photoencapsulation studies.

Wednesday 5:30 Founders Ballroom PO35

Rheological properties of starch, passion fruit and nanoclay based suspensions used in flexible films

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Polymers from natural sources have been recognized as an alternative to some environmental problems. The mesocarp flour of passion fruit (MF) was used to produce flexible films of cassava starch and to investigate the addition of clay as nanofiller, by varied characterization techniques. The films were made by a casting technique, from film-forming solutions (FFS) at 5% (w/w) of the total solids (cassava starch and/or MF) added with glycerol. The FFS were dehydrated to 30°C for 48h and the resulting films were kept in air relative humidity of 52.9% for six days. Rheological behavior of filmogenic solutions were carried out in a Thermo Haake rheometer MARS at 25°C, in order to classify the flow behavior and evaluate the influence of different matrices on viscosity. The apparent viscosity curves as a function of shear rate for each formulation showed a pseudoplastic behavior. The viscosity was higher for the filmogenic solutions based on MF. It was found that the addition of nanoparticles (NP) caused an increase in viscosity, especially for MF sample. The effect of MF and levels of nanoparticles on the viscosity at different shear rates was verified. It was noticed that there was an increase of 45% when NP were added to the mixture with 5% of MF, at a shear rate of 10 s-1. For filmogenic solution without MF (only starch), the addition of NP led to a 10% increase in viscosity. For a shear rate of 80 s-1, this difference was much smaller. The viscosity results obtained in each test were adjusted by the Ostwald-de-Waelle model. The parameters m and n for filmogenic solutions ranged from 1715.03 to 19964.88 Pa·s, and 0.41 to 0.84, respectively. With the addition of NP, we observed an increase in m for the suspensions based on MF. However, this fact did not occur to the suspensions produced only with starch.

Wednesday 5:30 Founders Ballroom PO36

Rheological study of mixed juices with functional properties

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The mixed juice with functional properties was developed from a mixture of Brazilian fruits, called a new age soft drink, that involves simultaneously taste, healthy, convenience, practical, and quality aspects. In order to project the pumping system with energy economy, it is very important to determine the flow characteristics of the mixed juice. Thus, shear rate sweep tests were carried out in a rheometer ARG2, TA Instruments, at 25°C, 70°C, 80°C, 90°C and 98°C. Flow curves were obtained for each temperature and the behavior was the same. Up to 500 s-1, shear stress curves were constant. There was a sharp decrease in viscosity with shear rate up to water viscosity value, for a shear stress equals to 10 Pa. From this point, the viscosity was constant.

Wednesday 5:30 Founders Ballroom PO37

Rheological behavior of molten lignin

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Lignin obtained from biofuel production wastes is a renewable material, non-toxic, that can be found in different biomasses. In Brazil, the most important biomasses are those from coconut, sugar cane bagasse, and paper industries. Biofuels can be obtained from different sources, such as vegetable oils and biomasses. Because of the concern about using food to produce fuels, there is an increasing interest in producing alcohol, called alcohol of second generation, from residual biomasses. Brazilian researchers are studying those processes by using sugar cane bagasse and paper industry waste. Lignin is a residue from this process and it can be used for different applications. The objective of this paper is to study the rheological behavior of the molten lignin that will be extruded through orifice diameters as low as 0.3 mm The influence of shear rate, temperature and time on the flow index of the molten lignin was investigated by using an extensional viscosity fixture in an ARES rheometer from TA Instruments.

Wednesday 5:30 Founders Ballroom PO38

Cellulase enzymes leveraged as micromechanical probes of cellulose surfaces

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Cellulose, the most common organic compound on Earth, is a regular polymer of glucose that can be deconstructed to constituent sugars, which are further processed to make renewable transportation fuels. Our model feedstock is corn stover, an agricultural residue, pretreated with dilute-acid to make the cellulose more susceptible to enzymatic hydrolysis. Previously, we have shown that pretreated corn stover (PCS) exhibits a significant yield stress that decreases with decreasing volume fraction (Φ). However, yield stress decreases up to an order of magnitude more as enzymes digest cellulose than PCS at comparable Φ. Though slurries with smaller mean particle diameters tended to have lower yield stresses, reducing particle size mechanically could not replicate the yield stress reduction of smaller particles produced from more severe pretreatments. Therefore, another factor, like inter-particle interactions, must play an important role in reducing yield stress and increasing susceptibility to enzymatic digestibility.

In this work, we use Cel7A enzymes as molecular probes for interrogating cellulose surfaces. Cel7A consists of a carbohydrate binding module (CBM) linked to a catalytic domain (CD). The CBM associates Cel7A with biomass, binding it to the surface. How much total Cel7A a substrate will adsorb is a first pass, but not complete, surface description and predictor of hydrolysis rate. The CD must find a reducing end of the cellulose chain and pull it from the crystal face to form a catalytically active, threaded complex. We developed a novel assay to differentiate between adsorbed and threaded Cel7A populations and couple it with well-characterized model cellulose substrates. The relative populations of threaded Cel7A correlate with predicted free energies of decrystallization for different crystalline polymorphs. We propose extending this method to a lignocellulose surface characterization measure to determine if they predict slurry properties, like digestibility and yield stress.

Wednesday 5:30 Founders Ballroom PO39

Structure and biodegradability of PLA and PBSA blend

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Aliphatic polyesters such as poly[(lactic acid)] (PLA) and poly[(butylene succinate-co-adipate)] (PBSA) have been widely used for biodegradable products. Limiting factors for a broader use of synthetic aliphatic polyesters are their poor mechanical properties. Synthesis of aliphatic polyesters was performed following the two-stage melt polycondensation method (esterification and polycondensation). Controlling the molecular weight of aliphatic polyesters is necessary to improve their mechanical properties. Polymer blending is also an effective way of achieving a desirable combination of properties, which are often absent in single component polymers. This work is composed of two parts. In the first part, we have optimized the reaction parameters of PBSA such as temperature of esterification and polycondensation, rotating speed of impeller, and reaction time to increase the molecular weight of PBSA. In the second part, we have measured the biodegradability of aliphatic polyesters. For PBSA homopolymer, the ratios of succinic acid (SA) to adipic acid (AA) were controlled to examine the effect of AA contents on the biodegradability. In the case of the PLA and PBSA blend, the blending ratios and the contents of organoclay were varied. The biodegradability of PBSA increased with increasing AA contents because of the decrease of the crystallinity of PBSA. The biodegradability of PLA/PBSA/organoclay composites for various blending ratios could be controlled by the contents of organocaly .

Wednesday 5:30 Founders Ballroom PO40

Extensional rheology of active suspensions of motile microbes

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We study extensional flows of low-viscosity aqueous microbial suspensions with a novel capillary-breakup device that uses surface acoustic waves to create observable liquid bridges rapidly from microliter-sized sessile droplets. In line with theoretical predictions (Saintillan, 2010), we observe that capillary breakup of filaments of live suspensions *E. coli* pushers is significantly faster than that of dead-cell suspensions, while for microalgal (*D. tertiolecta*) pullers, the behaviour is reversed.

Wednesday 5:30 Founders Ballroom PO41

Shear and uniaxial extensional rheometry of aqueous solutions of hydrophobically modified polysaccharides

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Most of the rheological studies on industrial polymeric fluids presented in the literature focus entirely on shear flows. However, many industrial and sensory processes are either dominated by, or at least have a significant component arising from extensional deformation - e.g. coating, atomisation and spraying, flow through porous media and swallowing in the case of food products.

Any comprehensive rheological characterisation of a polymeric rheology modifier should therefore include measurements by both shear and extensional rheometry. The present study considers the effects of hydrophobic modification on the rheology of aqueous solutions of hydroxyethyl cellulose by considering both the parent and alkyl substituted polymers. The results in both shear (linear and non-linear) and uniaxial extension (CaBER) are discussed in terms of the contribution of both hydrophobic associations and topological interactions to the dynamics and connectivity of the network.

In the *latter* experiments, both the magnitude of the uniaxial step strain and the 'strike time' associated with its imposition were varied systematically and the effect on the calculated timescale for viscoelastic stress growth and limiting extensional viscosity investigated. These data, augmented by high speed video imaging of the fluid filament, enabled an experimental window of operability to be established for the technique.

Normal stress behaviour for both polymers were compared using controlled rate peak hold experiments in order to establish the relationship between hydrophobic association and first normal stress difference.

Wednesday 5:30 Founders Ballroom PO42

Connecting large-amplitude shear rheology to unidirectional shear rheology and application to biomass slurries

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Large-amplitude oscillatory shear (LAOS) rheology has been the subject of intense study during the last decade. However, little work has been done to connect a material's response to oscillatory shear with the material's response to unidirectional shear (US). In this work we connect LAOS to US by employing constitutive equations that can be evaluated in both mathematical frameworks. Specifically, we used the Fourier transform formalism to analyze LAOS data for a material, and fit the resulting Fourier coefficients with those that result from an appropriate constitutive equation. The best-fit constitutive equation that resulted from the LAOS experiments was then compared to experimentally obtained US profiles. Model Newtonian, shear-thinning, and yield-stress materials were used as test materials. We propose that these methods are useful for determining the constitutive rheology of so-called problematic materials that are difficult to probe with traditional US rheometry methods (materials that experience fracture or ejection). In particular, we demonstrate the use of the approach to determine the bulk rheology of biomass slurries that arise during the biochemical conversion of biomass to fuel.

Wednesday 5:30 Founders Ballroom PO43

Preparation of spheroidal and ellipsoidal particles by extension of polymer films with spherical polymer particles

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Generation of particles of various sizes and shapes can be of great interest to scientists and engineers. We have developed a new apparatus which can induce biaxial extension of a film in an oil bath to generate particles with various shapes. PS suspension was prepared by dispersing PS particles in the aqueous solution of PVA. The suspension was poured into a pan and dried to form a film of thickness 250μm. The dried film was held by an eight-jaw extensional apparatus. The jaws were positioned in the edges of a regular octagon and moved radially to induce biaxial extension in an oil bath. The extended film was quenched in cold water and then the cooled film was dissolved in isopropanol-water mixture to collect the deformed particles using a centrifuge. The particles were washed several times with the mixture in the centrifuge and then the fluid remained in the interstices were removed in a vacuum dessicator to collect liquid free particles. The microscopic studies show that the oblate spheroids obtained by this method are virtually exact spheroids without showing knife edges. Also depending on positions with regard to holders ellipsoids and even prolate spheroids can be obtained. The method has been found to be robust in that the deformation is always reproducible regardless of film thickness. We have confirmed that this method can be applied for particles with submicrons to 10 micrometer in diameter. Considering the thickness of the dried film this method can be applied to particles of as large as 100μm. It is expected that the spheroids and ellipsoids obtained by this method can be of help in the study of rheology of suspensions of non-spherical particles.

Wednesday 5:30 Founders Ballroom PO44

Transient gels in development of polypropylene nanocomposites with polyhedral oligomeric silsesquioxane

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Nanoscale dispersion of polyhrdral oligomeric silsesquioxane (POSS) particles was produced in isotactic polypropylene (iPP) when dibenzylidene sorbitol (DBS) was used as a dispersion aid. DBS has been widely used as efficient nucleating agent of iPP. Under controlled cooling from the molten state, DBS crystallizes in the form of long fibrils and forms a transient gel in molten iPP. The stability of these gels, as well as the gelation temperature, is affected by the presence of other molecules or functional groups that may interact with DBS. The hydroxyl groups in the structure of DBS are capable of forming hydrogen bonds with other molecules, thus affecting the fibrillar structure and the strength of the transient gel. In this work, a silanol-POSS molecule with four Si-OH groups was dispersed in molten iPP in the presence of DBS and the nature of POSS-DBS interactions was investigated by rheological measurements. We report the results of a series of stress relaxation experiments with the gels. Relaxation modulus of viscoelastic fluids was characterized by a constant modulus a shorter times followed by flow at longer times. The constant modulus G0 was found to be a characteristic measure of the strength of the gel. In experiments, step strains 2% and 5% were used at temperatures between 160C and 200C. The values of G0 of iPP/DBS gels were found to be respectively 9000, 8300, and 3400 dyn/cm2 at 160C, 170C, and 180C, while the values of G0 of iPP/DBS/POSS gels were much higher, respectively 116000, 34900, and 1600 dyn/cm2 at the same temperatures. Higher values of G0 in latter case may be attributed to four -OH groups of POSS molecule interacting with DBS via hydrogen bonding. However, at 180 ?C, the lower value of modulus was due to POSS restricting the ability of DBS to form gels. It was possible to conclude from these data the different relaxation mechanisms that took place in these gels.

Wednesday 5:30 Founders Ballroom PO45

Reversible photorheological fluids induced by transition between vesicles and wormlike micelles

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Fluids whose rheological properties, such as viscosity, can be tuned by light are of interest to scientists and engineers. Such fluids can be termed photorheological (PR) fluids. Because light can be directed at a precise point with a resolution on the order of microns, PR fluids may be useful in microscale or nanoscale devices as the basis for valves or flow sensors. Other applications have also been envisioned for PR fluids, e.g., as drag-reducing fluids in recirculating systems for district heating and cooling, in microrobotics, and as patternable materials. However, in most cases, the synthesis of complex photosensitive molecules is required in order to create PR fluids. Due to such chemical synthesis, the widespread use of these fluids is hindered. In our research, we are working toward simple classes of PR fluids that require no special synthesis and can thereby be easily replicated in any laboratory from inexpensive chemicals. Several examples of simple PR fluids have been published recently from our laboratory; however, all these fluids permitted only 1-way changes in rheological properties. Here, We show simple reversible PR fluids based upon combining an azobenzene derivative, 4-azobenzene carboxylic acid (ACA), into micelles of the cationic surfactant erucyl bis(2-hydroxyethyl)methyl ammonium chloride (EHAC). At certain concentrations of EHAC/ACA samples, we have found an increase in viscosity upon UV irradiation, which correlates with a trans to cis photoisomerization. In addition, when the sample is exposed to subsequent visible light, we have observed a decrease in viscosity, which corresponds to a cis to trans reverse photoisomerization. The resultant change in the geometry of ACA alters the molecular packing of the EHAC/ACA complex, inducing reversible transition between vesicles and wormlike micelles. This change in viscosity can be repeated, leading to a substantial reversible change in viscosity that can be cycled many times over.

Wednesday 5:30 Founders Ballroom PO46

Structural and rheological investigation of fully hydrated fibrin gels: An in-situ neutron scattering study of structural transitions under shear deformation

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Fibrin is a protein that self-assembles into a bifurcating nanofibrous network forming the primary structural component of a blood clot. Developing relationships between the mechanical and structural properties of fibrin clots is critical to the diagnosis and treatment of various clotting conditions. Using small angle neutron scattering (SANS) and rheological techniques we seamlessly characterize the structural and mechanical properties of fully hydrated fibrin gels. Like many other biopolymers, fibrin gels are highly elastic and stiffen when deformed. Though several theoretical models exist that describe the strain-hardening of semi-flexible biopolymer gels, the origin of this phenomenon is, as of yet, not fully understood. SANS is used to directly probe the structural properties of fibrin as the gel is deformed. The results of this study indicate that as fibrin is strained it undergoes critical mechanical transformations that are directly linked to the underlying structure of the gel.

Wednesday 5:30 Founders Ballroom PO47

A study of flow-induced structure formation in wormlike micellar solutions using local micellar concentration measurements

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Wormlike micellar solutions exhibit a wide variety of phenomena, one of which is the formation of flow-induced gel-like structures. In some cases these structures are temporary and disintegrate upon cessation of the flow, in other cases these structures can be stable and very long-lived. Here, we present a series of experiments examining flow-induced structure formation in microfluidic flows of a micellar solution using the fluorescent dye Nile red. By using Nile Red, we are able to examine and measure the local micelle concentration of the solution under purely shear flows and mixed (shear and extensional) flows. We find that in mixed flows local concentration variations up to ~ 10% are observed during flow in cycles, while in purely shear flows no measurable concentration variations are observed. We have also investigated how these flow-induced micelle concentration variations are related to the formation of the flow-induced structures previously reported in the literature.

Wednesday 5:30 Founders Ballroom PO48

Development of gel-structure in silica/PVA suspension during mixing

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The rheology of filled polymer system is of great importance because of its broad usage in many industrial applications. But adding particles to a viscoelastic fluid increases the rheological complexity of the system, which often leads to the formation of particular microstructure. Gel-like structure is one example. One of the reasons that form such a complex structure is the development of networks between the particles and polymers. This structural change may happen slowly during mixing because the interactions between particles and polymers, such as absorbing and bridging, might be developed for a long time of about 100hrs. So they show time-dependent structural change, so called aging. It can be a cause of serious defects in processing. But it is not easy to explain exactly why they form networks and gel-like structure because there are many variables which have to be considered altogether; mixing time, concentration of particle and polymer, pH and mixing intensity and so on. So In this talk, we will show the time-dependent microstructural change and rheological behavior of silica/PVA suspension which was selected as a model fluid. The effect of mixing time and concentrations of polymer on the suspension will also be discussed.

Wednesday 5:30 Founders Ballroom PO49

Self-assembled multicomponent plasmonic nanogels: Structure, rheology and optical properties

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Metallic nanoparticles in solution are unstable and tend to agglomerate leading to phase separation, thereby losing their unique electronic and optical properties. In this study, self-assembly in wormlike micelle (WLM) solutions is used to distribute various metallic nanoparticles to produce stable plasmonic nanogels with exceptional color uniformity [Cong et al., Applied Physics Letters, 99, 043112 (2011)]. The optical properties of the gels can be easily tuned by varying the type, shape and/or concentration of nanoparticles. In particular, multicomponent gels capable of broadband absorption of visible light can be robustly manufactured via the self-assembly route. Small angle X-ray scattering and rheological studies suggest that the nanoparticles materially participate in the WLM network to form a more compact double network. Such plasmonic gels exhibit rich rheological behavior depending on the nanoparticle concentration and the salt/surfactant ratio. Specifically, the gels show shear thickening, rheopectic and shear thinning behaviors as nanoparticle concentration is progressively increased. The nanogels exhibit enhanced viscoelasticity upon the addition of more nanoparticles and are thermoreversible. The mechanisms contributing to the rheological and optical properties of the plasmonic nanogels as well as their potential applications to efficient light trapping in photovoltaic cells and opto-fluidic devices will be discussed.

Wednesday 5:30 Founders Ballroom PO50

Elucidation of the structure and mechanical properties of ABA triblock copolymer hydrogels formed through complex coacervation

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We have found that equimolar mixtures of ABA triblock copolyelectrolytes bearing either guanidinium or sulfonate groups on the end blocks form responsive hydrogels when mixed together in water. This gelation is driven by the physical association and phase separation of the oppositely charged endblocks to form complex coacervate domains linked by water soluble polymer midblocks. This ionic physical domain crosslinking endows interesting properties to the materials, including the ability to form equilibrium structures with a responsive nature. We have investigated through rheology, SAXS, and SANS the structure and mechanical properties of the hydrogels as influenced by polymer concentration, salt concentration, pH, stoichiometry and temperature. While weak disordered physical gels form at concentrations as low as 6 wt%, at concentrations above 15 wt%, the gels strengthen by virtue of an ordered BCC network structure of the coacervate domains. The addition of salt causes ionic screening of the electrostatic interactions holding the structure together and eventually dissolves the gel. Finally, we have demonstrated that these hydrogels rapidly regain their mechanical properties within seconds after large strains have disrupted the network. Such properties position these hydrogels well as scaffolds for injectable drug delivery systems and biomedical devices.

Wednesday 5:30 Founders Ballroom PO51

Low-frequency dielectrophoretic response of a single particle in aqueous suspensions

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Alpha-relaxation, the counterion diffusion in the electric double layer at the interface of a colloidal particle and its surrounding medium, has been used to describe the anomalous low frequency dielectric dispersion of aqueous suspensions of colloidal particles. A microscopic theory describing this relaxation process proposed by Schwarz, however, has not been investigated systematically. We use an optical tweezers-based single-particle dielectrophoretic (DEP) force spectroscopy to study the relaxation mechanism as a function of particles size, temperature and solvent viscosity. Specifically, we measure the dependence of the DEP crossover frequency and compare results with predictions by Schwarz.

Wednesday 5:30 Founders Ballroom PO52

Novel approaches to interfacial dilatational rheology

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Whereas methods for interfacial shear rheology are readily available, methods for probing the rheological material functions in dilatation are not that well established. In the present work we analyze some of the existing methods such as Langmuir throughs with oscillating barriers and the oscillating drop technique. We introduce some new tools for interfacial rheology, including a Double Wall Sinusoidal Ring which can be coupled to a rotational rheometer. We will also investigate if a radial trough can be used to sudy the dilation. Results in both fatty acids and particle laden interfaces will be presented.

Wednesday 5:30 Founders Ballroom PO53

A study on relaxation time spectrum and linear viscoelasticity of interface

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We studied the effect of interface on linear viscoelasticity of immiscible polymer blends. We calculate weighted relaxation spectrum of polymer blends to detect the effect of interface because it is known that weighted relaxation spectrum shows a peak which can be assigned to interfacial effect. The height and the relaxation time for the peak are dependent on several factors such as the concentration and size of disperse phase, interfacial tension, and viscosities of the ingredients. It was reported that the relaxation spectrum is better than other methods in quantitative analysis of interfacial behaviors. However, determination of relaxation spectrum is sensitive for experimental errors in rheological data due to the ill-posed problem. We tested a few algorithms of relaxation time spectrum for the detection of the interfacial behavior with several kinds of rheological data: immiscible polymer blends, melt of rubber toughened polymer (ABS) and immiscible mixtures of viscous fluids.

Wednesday 5:30 Founders Ballroom PO54

Interfacial effects on droplet dynamics in Poiseuille flow

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Many properties of emulsions arise from interfacial rheology, but a theoretical understanding of the effect of interfacial viscosities on droplet dynamics is lacking. Here we report such a theory, relating to isolated spherical drops in a Poiseuille flow. Stokes flow is assumed in the bulk phases, and a jump in hydrodynamic stress at the interface is balanced by Marangoni forces (linearized with respect to local deviations of interfacial surfactant concentration) and surface viscous forces according to the Boussinesq-Scriven constitutive law. Interfacial diffusion is also included. Our analysis predicts slip, cross-stream migration and droplet-circulation velocities. These results and the corresponding interfacial parameters are separable: e.g., cross-stream migration occurs only if gradients in surfactant concentration are present; slip velocity depends on viscosity contrast and dilatational properties, but not on shear Boussinesq number. This separability allows a new and advantageous means to measure surface viscous and elastic forces directly from the drop interface. Modeling of other geometries will also be discussed.

Wednesday 5:30 Founders Ballroom PO55

The study of surface behavior of novel sodium dodecyl sulfate (SDS)/ polyethyleneimine (PEI) complex

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Novel surfactant/polyelectrolyte complexes have been the focus of recent research efforts due to their applications in consumer products, petroleum engineering and biotechnology. We report on surface activity of SDS/PEI surfactant/polymer complex. Particle size distribution, zeta potential and entrapment efficiency were determined to investigate the properties of SDS/PEI complexes, while a Langmuir trough and a recently developed interfacial microrheometer are used to test their interfacial properties. Results suggested that the presence of PEI/SDS mixture reduced the surface tension at air/solution interface compare to pure SDS solution. However, the resuspended complex with no free SDS showed little surface activity in the surface tension measurements.

Wednesday 5:30 Founders Ballroom PO56

Time-resolved small-angle x-ray scattering studies of shear-induced orientation in wormlike micelle solutions subjected to step-strain deformation

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Wormlike micelles of cationic surfactant micelles in aqueous solution have attracted considerable attention in light of the nearly single-exponential relaxation modulus they frequently exhibit, and many similarities in nonlinear rheology with entangled flexible polymers. However, certain wormlike micelle formulations exhibit nonlinear rheology that is markedly different from entangled polymers. In particular, solutions of cetyltrimethylammonium bromide (CTAB) in the presence of sodium salicylate (NaSal) frequently exhibit strain hardening of the relaxation modulus measured in step-strain deformation. Here we present x-ray scattering measurements of micellar orientation induced by step-strain, and its relaxation, in several aqueous CTAB/NaSal solutions. Small-angle x-ray scattering measurements were performed using an annular cone and plate shear cell which allows measurements of the degree and direction of micellar orientation in the flow-gradient plane of shear flow. Studies of structural dynamics were facilitated by the use of synchrotron radiation and a fast CCD detector, as well as the relatively long relaxation times found in the test solutions. The degree of micellar orientation increases as a function of applied strain, while the orientation angle decreases towards 0° with increasing strain. The orientation angle is constant during relaxation, and its magnitude follows expectations for affine deformation of fluid structure during the applied step-strain deformation.

Wednesday 5:30 Founders Ballroom PO57

Microstructure, crystallization, and rheology of a model crystallizing surfactant system

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Complex fluids with high concentrations of crystallizing fatty acids are important for consumer care products. These fluids demonstrate solid-like elastic behavior at rest but yield and flow under an applied strain. Such behavior is characteristic of isotropic, space-filling networks. The crystallization process determines the microstructure of these systems, which in turn influences their macroscopic rheological properties. A combination of methods, including differential scanning calorimetry (DSC), proton Nuclear Magnetic Resonance (pNMR), X-ray scattering, optical microscopy, and rheology, utilized in this research provides a framework for understanding crystallizing systems. The kinetics of crystal growth in model compositions comprising (by mass) 9% sodium dodecyl sulfate, 3% cocamidopropyl betaine, and different specified amounts of palmitic acid in water or deuterated water, were studied using pNMR and DSC. The Avrami exponent value was approximately 2.0 for formulations with 11% and greater amounts of palmitic acid. Considering the anisometry of the crystals evident via microscopy and the development of crystals in formulations with 5 and 7% palmitic acid in less than one week, it is reasonable to assume 2D growing dimensions and a mechanism of crystal growth control via diffusion and surface incorporation. A minimum of 5-7 wt% of fatty acid is required to achieve the formation of a percolating crystal network. The storage modulus, yield stress and strain of these formulations show a non-monotonic increase with fatty acid content. This is attributed to the change in the fatty acid crystal habit from large to small aspect ratio plates. We hypothesize that the fatty acid crystal network consists of crystal aggregates linked by surfactant-fatty acid gels, rendering the desired paste-like characteristics to the formulation. Network formation is also influenced by the ionization states of the palmitic acid and cocamidopropyl betaine.

Wednesday 5:30 Founders Ballroom PO58

Additive turbulent drag reduction in high shear flow

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High shear drag reduction due to additives was experimentally investigated in a turbulent tube flow. The tube diameter was 0.90 to 5.96 mm. The cationic surfactant was combined with the counter ion of equi-molar to thirty times higher molar concentration. The high concentration of the counter ion enhanced the drag reduction at high Reynolds number, and the surfactant solution indicated the drag reduction of 50% at the shear stress of 100 Pa. Other than the surfactant solutions, the dispersed systems of nanotubes and potassium titanate whiskers were investigated. These additives increased the viscosity, but the frictional increase due to the viscosity was not observed. However, the drag reduction was not obtained compared with the friction of dispersing water. The conditions of the concentration and the tube diameter must be investigated for these dispersed systems of solid particles to achieve more effective drag reduction.

Wednesday 5:30 Founders Ballroom PO59

A comparison of the quiescent stability and structural rearrangement of particle-stabilized and surfactant-stabilized 2D foams

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Foams are often utilized in a wide range of industrial processes, including the production of solid foam structures formed through polymerization or freezing. Of key importance in these applications is understanding not only the stability of liquid foams, but also the susceptibility of the foam geometry to structural rearrangements that can occur over time. These bulk foam properties are a direct result of the rheology of the gas-liquid interface. Standard methods of testing foam stability are difficult to relate to interfacial rheological properties, and techniques used to measure the structure of foams, such as light scattering, are often frustrated by the turbid nature of 3D bulk foams. Using microfluidic tools, we will study the interfacial properties of nanoparticle systems in comparison with standard surfactant systems and relate those properties to foam structure and stability. In order to study the dynamic surface tension and interfacial elasticity of small (radius ~10-5 m) bubbles, we will use a microtensiometer capable of measuring adsorption to the highly-curved interfaces inherent in microfluidic systems. In tandem with these experiments, we will generate monodisperse foams stabilized by nanoparticles in a microfluidic device and compare those to surfactant-stabilized foams generated using similar techniques. We will observe the stability of these foams under quiescent conditions as well as the rearrangements that occur in the foam structure over time, and draw comparisons between the interfacial properties and the observed phenomena.

Wednesday 5:30 Founders Ballroom PO60

A quantitative analysis of the effect of viscosity ratio on droplet formation and mixing in a μ^2rheology device

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Recently, the combination of microrheology measurements with microfluidic sample processing, or μ^2rheology, has enabled rapid characterization of scarce and expensive materials over a large composition space [1]. However, like many microfluidic applications, mixing of different materials in a droplet becomes a critical issue in the performance of μ^2rheology. One of the most common methods of mixing in microfluidic experiments is passive mixing, which relies on the diffusion of molecules in the droplets due to concentration gradient. But whether through mixing of materials with different viscosities can occur in a drop has been questioned due to the differences in the diffusion coefficients. In the present research, a microchannel with a T-junction inlet followed with a series of straight channels in the millimeter-scale is fabricated using the standard soft-lithography method to analyze the internal motion of a drop. A set of two water streams and a stream set of water and 75 vol% of glycerin solution in water are chosen to compare viscosity ratio effect. The streams are dyed in different colors and the Lagrangian movies are generated from the recorded image sets. The Lagrangian movies show the change in the internal motion of droplet as it forms and travels in the microfluidic device. The pixel intensity is extracted to quantify the motion of the materials for the horizontal axis and vertical axis. The color profile for the drop composed of materials with a viscosity ratio of higher than one levels off over time. Otherwise, the pixel intensity change shows that the two different materials with a viscosity ratio of one tend to be captured in each side of the dipolar vortex. Here, the arrangement of materials plays an important role in mixing and the mechanism of the material arrangement at the T-junction is a matter of the fluid mechanics. In addition, the microchannel with chaotic advections is studied quantitatively for comparison

[1] K. M. Schultz and E. M. Furst, Lab Chip, in press.

Wednesday 5:30 Founders Ballroom PO61

Determination of intrinsic viscosity using a viscometer for prediction of minimum fiber diameter in electrospinning

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Knowledge of the intrinsic viscosity ([η]) of polymer solutions is essential in order to obtain the viscosity averaged molecular weight (Mv), yet also useful to shed light on appropriate conditions for electrospinning of polymer solutions. In the latter, optimal chain entanglement is desired. In our experience, the product [η]c (referred to as the Berry number) should be 5 or greater for droplet-free electrospinning of fibers, while increasing the concentration too high will lead to undesirably large fiber diameters. Consequently, Mv should be large enough (and thus [η] large enough) to allow this condition to be met at low concentration. The conventional technique of Ubbelohde viscometry to measure intrinsic viscosity is laborious and intrinsically yields kinematic viscosity. We sought an easier method that would directly measure viscosity without solvent evaporation concerns and, by virtue of simplicity, allow facile exploration of the dependence of intrinsic viscosity on mixed solvent compositions. Using the m-VROC, a chip viscometer, from Rheosense, Inc., we measured the isothermal viscosities of low concentration polymer solutions for a range of concentrations. The intrinsic viscosity could then be determined by linear regression of the Huggins and/or Kraemer plots. In this report, we will detail the measurement methodology to yield intrinsic viscosity for several polymer/solvent systems, including poly(vinyl acetate) in methanol, and correlate these findings with the onset of droplet formation in electrospinning of the same solutions with decreasing concentration.

Wednesday 5:30 Founders Ballroom PO62

Deformation of CNT dispersing drop in a 4:1 microfluidic contraction channel

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The dispersion of carbon nanotube (CNT) to polymer melt is successfully accomplished by masterbatch (concentrated CNT dispersion) dilution method. To investigate how the concentrated CNT dispersion (CNT master) phase is dispersed to polymeric matrix, the formation of CNT dispersing aqueous drop (0.5wt%CNT/2wt%alginic acid solution) in oil environment (polydimethylsiloxane) was carried out in a flow-focusing microfluidic channel (0.5 < flow ratio of center and side flow < 3, center flow ~ 2ul/min, 4ul/min). Also, we observed the deformation of CNT dispersing aqueous drop in a 4:1 contraction microchannel (contraction width=100um, depth of channel = 100um). When the drop generated at the flow focusing channel, the size of CNT dispersing drop is larger than that of the aqueous solution without CNT due to higher viscosity. As flow ratio increases, the difference in drop size induced by CNT dispersion decreased due to shear thinning behavior of CNT dispersing aqueous solution. During passing a contraction channel, heterogeneously dispersed CNT aggregate in an aqueous drop induced drop deformation as well as breakup. Though CNT thermodynamically prefer oil phase to aqueous phase, CNT did not migrate from drop phase to matrix during passing through channel. We surmise that the CNT dispersion by masterbatch dilution method does not occurred by CNT migration, but by active drop breakup of CNT master phase.

Wednesday 5:30 Founders Ballroom PO63

Numerical simulation of non-Newtonian fluid flows in double concentric cylinder rheometer with slotted rotor and vane rheometer

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Wall slip effects can be effectively reduced in a double concentric cylinder rheometer with slotted rotor (DCCR/SR). This suggests that the DCCR/SR is a potential alternative to a vane rheometer for yield stress measurements. Here, we use three-dimensional computational fluid dynamics (CFD) simulations to compare these two designs for rheological measurements of power law and yield stress fluids. Three major factors related to the total systematic error are analyzed independently for both geometries: wall slip effects, end effects and secondary flow effects. Our results indicate that: (1) Wall slip effects are relatively constant for the DCCR/SR but increase with the power law index in the case of a vane rheometer; (2) End effects and secondary flow effects are stronger in a vane rheometer than in the DCCR/SR; (3) for yield stress fluids the DCCR/SR design achieves a higher measurement accuracy than a vane rheometer.

Wednesday 5:30 Founders Ballroom PO64

Numerical simulation of giant intracranial aneurysm embolization with a yield stress fluid material

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The endovascular treatment of intracranial aneurysms remains a challenge, especially when the aneurysm is large in size and has irregular, non-spherical geometry. Here, we use computational fluid dynamics to simulate blood flow in a vertebro-basilar junction giant aneurysm. Based on the geometry reconstructed from a cadaveric specimen, three cases were considered: 1) an empty aneurysm, 2) an aneurysm filled with platinum coils, and 3) an aneurysm filled with a yield stress fluid material. In the computational model, blood and the coil-filled region are treated as a non-Newtonian fluid and an isotropic porous medium, respectively. The results show that 1) yield stress fluids can be used for aneurysm embolization provided the yield stress value is 20 Pa or higher, 2) there exists a strong flow recirculation in the empty aneurysm which is reduced by coil treatment but can be minimized by yield stress fluid treatment, and 3) the size of the inflow jet impingement zone on the aneurysm wall is reduced most considerably when the aneurysm is filled with a yield stress fluid material. Overall, this study opens up the possibility of using yield stress fluids for effective embolization of giant intracranial aneurysms.

Wednesday 5:30 Founders Ballroom PO65

Brownian dynamics simulation of large amplitude oscillatory shear flow of repulsive colloidal particle suspensions

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Recently, interest on the structure formation of colloidal particle suspensions under large amplitude oscillatory shear (LAOS) flow has been increased. However, direct observation of colloidal particles in experiments is hardly accessible due to the limitation on resolution of optical techniques and relatively small scale for whole structure. To overcome this problem, we used Brownian dynamics (BD) simulation technique to get an information of the micro-structure and rheological properties. In our simulation, repulsive suspensions were used, and we investigated the effect of volume fraction, strain amplitude and Deborah number (De) of the suspension. A strain sweep test was then performed to randomly dispersed 1000 particles at every 10% of strain amplitude, and we obtained representative stress signals in which 30 cycle's stress outcome was

averaged in same strain amplitude . To analyze this stress response, we used a stress decomposition method which divides the total shear stress into elastic and viscous contribution. In our BD simulation, the stress decomposition shows that the viscous shear stress is dominant in low volume fraction region. In high volume fraction region, the total stress curve shows tilted shape when the strain amplitude and De increase and this result will be related with the dramatic micro-structure change of the colloidal particle suspensions in LAOS region.

Wednesday 5:30 Founders Ballroom PO66

Rheological properties and microstructure of 10:1 bimodal dispersions under simple shear

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The rheological properties and microstructure of bimodally distributed particle suspensions were investigated using Brownian dynamics simulation. The rheological properties were determined by changing the volume fraction of small particles from 5% to 20%, fixing the volume fraction of large particles at 20%. To properly consider the interparticle forces between colloidal particles, we used accurate analytic formulas for the double-layer interaction between spheres which come from the Poisson-Boltzmann equation for two spheres(JOHN E.Sader et al,J.Colloid Interface Sci.,(1995),171). The interparticle force between the particles was given as attractive, except the interaction between large particles, where repulsive force was imposed. The size ratio of big and small particles was in between 10 to 1. We applied simple shear flow in the range of 0.001~10 dimensionless shear rate, and compared the difference of rheological properties between mono-dispersed system and bimodal system. The bimodally distributed suspensions showed different rheological properties in comparison with those of mono-dispersed one. And we could observe the microstructural changes of the small particles around the large particle at given shear rate and volume fraction. In this work, we tried to analyze the microstructure of bimodal dispersions by using pair distribution function, time average number density.

Wednesday 5:30 Founders Ballroom PO67

Modeling of solute-exclusion zone: A dissipative particle dynamics study

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The discovery of a large solute-exclusion zone in water, in the range of tens to hundreds of microns, occurring between functionalized microspheres and hydrophilic polymer gels has sparked the interest of many researchers [1-3]. Currently, there is a lack of understanding as to why this exclusion zone forms and is so large. Some possible explanations including electrostatic repulsion and/or water molecules ordering past nanometers have been proposed [4,5] but have yet to be confirmed experimentally. To understand and properly characterize this phenomenon, dissipative particle dynamics (DPD), a molecular simulation method, [6-9] was employed to mimic it [10]. Initial DPD simulations showed the creation of a solute-free zone of 12 μm between a polymer gel surface and colloidal particles with a volume fraction of 30 % of the colloidal particles in water. There are also promising results seen at 10 vol% of microspheres suspended in water. Further work with parameter sensitivity simulations is underway to determine which parameter(s) is/are responsible for the exclusion zone size and the results will be presented.

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Wednesday 5:30 Founders Ballroom PO68

Simulation of rheological properties of liposomes

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Liposomes are commonly used as a delivery system for medicinal and vaccine purposes. They are enclosed bilayers made from a variety of phospholipids and cholesterols. In this work we make use of a red blood Cell evolution equation in mathematical biology to define liposome deformation and aggregation. The mathematical equation used successfully fits the experimental data known in literature. The coupling parameters involved in the expression of the time dependent viscosity of the liposome have been calculated. A figure representing the graph of the evolution of the liposome viscosity with respect to the shear rate will be shown.

Wednesday 5:30 Founders Ballroom PO69

Mesoscale simulation of colloidal particles during drying process

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Drying process is a key issue in some industrial applications such as fabrication of electronic devices. It is well known that the quality of a final product is strongly correlated with the packing structure of the particles, which is formed during drying process. In drying process, the particle structure depends on various factors such as evaporation rate, interfacial tension, temperature, and so on. Even though real situation is much more complicated, a numerical simulation approach can be useful in understanding the drying mechanism and estimating the optimum process window. The main difficulty in drying simulation is that we have to consider both hydrodynamic interaction and interfacial tension among colloidal particles and fluids. As a promising tool to study this complex system, several mesoscale simulation techniques have been introduced in recent years. We adopted Lattice Boltzmann method (LBM) which is one of the mesoscale simulation schemes. In this simulation study, we focused on the structure formation of nearly hard spheres during drying process. We changed drying conditions such as the volume fraction of colloidal particle and evaporation rates of solvent. During drying process, we observed crystallized structure of colloidal particles, which is induced by capillary driven pressure near fluid interface. Finally, this packing structure of colloidal particles was quantitatively analyzed in terms of pair correlation function, bond number distribution, and Q6 order parameter.

Wednesday 5:30 Founders Ballroom PO70

Mesoscopic simulation of co-polymeric systems: DPD and MDPD approach

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Dissipative Particle Dynamics (DPD) is a promising simulation method for soft matters, including colloidal suspensions, polymer solutions, polymer melts, polymer blends and polymer nano composites. Simulation of complex by DPD has been found to be problematic, so in order to improve the original formulation different models such as Core-Modified DPD method [1], Coarse-Grained Level Tunable DPD method [2] and Multi-body Dissipative Particle Dynamics (MDPD) [3] have been proposed. MDPD was originally proposed to discuss mainly liquid-vapor systems [3]. Formulation of the conservative force in MDPD, using the local density information in pairwise particle interaction, enables a more accurate prescription of thermodynamic behavior in interacting systems; hence, MDPD shows strong potential to discuss dynamics of polymer blend and co-polymeric system. However, there is no report on this type of systems in the literature. Furthermore, no relation between Flory-Huggins parameters and that of MDPD has been proposed so far. The main objective of the present work is to establish a simulation method for polymer blends and co-polymeric systems by MDPD. The relation between Flory-Huggins parameters and MDPD parameters was decided based on Groot and Warren method [4] by comparing predictions of MDPD and DPD in terms of interfacial tension, calculated from Irving Kirkwood formulation [5]. In this work, we mainly discuss the method to decide parameters, stability of interfaces and dynamics of co-polymeric systems

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Wednesday 5:30 Founders Ballroom PO71

A study on the flow instabilities in multiplier dies through direct visualization and flow simulation

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Recent advances in layer-multiplying coextrusion of incompatible polymers have made possible to fabricate multilayered nanostructures with improved barrier, thermal and mechanical behavior. However, when the differences between the viscosity and/or elasticity of the coextruded materials are relatively high, flow instabilities arise during the processing, which leads to non-uniform layers and non useful multilayered films. In this work, the flow patterns in the multiplier dies was investigated using both direct visualization and flow simulations using Polyflow. A new modular multiplier die, which allows the cooled materials from inside to be removed in whole sections, was used. These sections are divided and the extrudates studied to observe the formation of the flow instabilities and how different extrusion variables effect their formation. The flow simulation is used as a comparison tool to validate the accuracy of predicting the formation and continuation of flow instabilities.

Wednesday 5:30 Founders Ballroom PO72

Non-monotonic stretch of isolated semiflexible polymer chains in ultra-fast shear flow

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We investigate the stretching behavior of semiflexible polymers in shear flow using Brownian dynamics simulations. For the polymer chain we use a bead-spring model that uses a harmonic bending potential between springs to mimic the continuous bending characteristic of semiflexible polymers. Simulations run over a range of shear rates from low to ultra-high show that the behavior of the semiflexible model is qualitatively similar to the behavior of flexible polymer models used by Indranil Saha Dalal and Ronald G. Larson in their soon-to-be-submitted work to the Journal of Rheology. Similar to the results presented by Dalal et al. for flexible chains, we see three distinct regimes of polymer stretch for semiflexible polymers. Like the flexible models the semiflexible model shows an initial increase in stretch at low shear rates ($Pe < 1$), a plateau in stretch at intermediate shear rates ($1 < Pe < 1000$), and finally a decrease in stretch at ultra-high shear rates (ie $Pe > 1000$). However, the onset of the decrease in stretch is delayed by an order of magnitude from the flexible chains. The semiflexible chains also show scaling laws quantitatively similar to flexible chains in the vorticity and gradient directions. For Dalal et al.'s flexible model, hydrodynamic interactions (HI) and excluded volume (EV) were neglected and could have strong effects due to the strong self-interactions of a freely-jointed chain. Our semiflexible model also neglected HI and EV, however, previous work [see summary in The rheology of dilute solutions of flexible polymers: Progress and problems; Larson, R. G., Journal of Rheology, 2005] has shown that HI and EV have lesser effects on semiflexible chains than flexible chains. This new work then shows that the presence of distinct regimes at high shear rates is more robust than previously believed.

Wednesday 5:30 Founders Ballroom PO73

Migration of particles in slit flow of suspension by 1-D simulation

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The flow dynamics and particle migration in particulate suspension systems have been extensively applied for the many precise industrial products such as slurries for long-life secondary batteries, ceramics with high modulus and functional particle layers on a polymeric film. It is thus of great interest to understand hydrodynamic interaction and concentration distribution of particles in the suspension under flow conditions. In this study, the one-dimensional diffusive flux model for Newtonian suspension developed by Phillips et al. (1992) was extended to develop the equation for non-Newtonian Carreau-type fluids in slit flow region where is featured by the combination of drag and pressure-driven forces. Effects of various conditions such as initial concentration and shear-thinning have been investigated.

Wednesday 5:30 Founders Ballroom PO74

Problem analysis of coarse-grained level tunable dissipative particle dynamics method

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Our group recently proposed a coarse-grained level Dissipative Particle Dynamics (DPD) method for entangled polymeric systems [1]. The method can reproduce reasonably both linear viscoelastic (transition from Rouse behavior to reptation behaviors with molecular weight) and non-linear viscoelastic behaviors (shear-thinning properties, first and second normal stress difference coefficients). One well-known problem of DPD simulation is the fact that a Schmidt number typical of gaseous systems is found in fluids fluids. So far, different methods have been proposed to resolve this problem. Lowe [2] introduced an alternative scheme for DPD based on Andersen's thermostat. Another method is to eliminate the time step effect [3] which stated that the Schmidt number problem is a result of the high coarse-graining level and is an intrinsic problem of the system that cannot be solved. On the other hand, employing the latter scheme gives a better accuracy for time integrating method and makes the method work precisely for larger time steps. The main objective of this work is to focus on the problem of CG tunable DPD method for polymeric systems. In particular, we focus on the Schmidt number problem and on increasing the DPD particle density to improve upon our recent results, especially in what concerns the dependency of the relaxation time on molecular weight.

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Wednesday 5:30 Founders Ballroom PO75

A modified version of the tube model to include flow-induced disentanglements in monodisperse entangled polymer melts under extension

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Recent slip link simulations of entangled polymers in extensional flow by Kushwaha and Shaqfeh [J. Rheol. 55(3), 463-483, 2011] show disagreement with classical tube theory in that they show flow-induced disentanglement and delay of extension hardening to strain rates higher than the inverse Rouse time. We have therefore incorporated flow-induced disentanglement and flow-induced reduction in the stretch relaxation time into the tube model to study the effects on the extensional rheology of monodisperse polymers. To incorporate flow-induced disentanglement, we have developed a functional form for the reptation time as a function of the tube orientation tensor, S, that is motivated by the theory of entangled rodlike polymers which show tube dilation and flow induced disentanglement under fast flow [Doi, M., and S. F. Edwards, The Theory of Polymer Dynamics, Oxford University Press, Oxford, UK, 1986]. Our functional forms for the reptation time and stretch time were adjusted to get the best possible fit to slip link data on disentanglement and extensional viscosity. This allows us to interpret the slip-link simulation results in terms of a modified tube model. A molecular explanation of the phenomena remains to be developed, however.

Wednesday 5:30 Founders Ballroom PO76

Linear and non-linear melt rheology of thermoplastic polyurethane /multi-walled carbon nanotube nanocomposites

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The aim of this work was to employ rheological techniques to study the microstructure development, and the dispersion state of Multi-Walled Carbon Nanotube (MWNT) in Thermoplastic Polyurethane(TPU) matrix. The TPU/MWNT nanocomposites varying in MWNT content (0.01%wt to 3%wt) were prepared by melt compounding. The linear viscoelastic results obtained from oscillatory tests showed a strong low frequency non-terminal storage modulus along with viscosity up-turn whose extent were found to be enhanced by increasing MWNT content. This solid-body response was a justifiable indication of a strong three dimensional network due to nano-nano and nano-matrix interconnectivity. Surprisingly, the rheological percolation threshold was discovered 0.15%wt which evidenced the great capability of Thermoplastic Polyurethane matrix in dispersion of MWNT. Results of non-linear viscoelastic tests in rotational state showed a pronounced shear dependency of the 3D network. Evolution of MWNT network structure was traced after start-up of steady shear flow experiment by storage modulus recovery experiment. Flow curve experiment indicated reduction of Newtonian region as well as elevation of shear thinning slope by increasing the extent of MWNT.

Wednesday 5:30 Founders Ballroom PO77

A rheological study on the mutual diffusion between co-extruded soft and hard thermoplastic polyurethanes

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By coupling a co-extrusion feedblock with interfacial surface generators, known as multiplying dies, it is possible to format two or more polymers into microlayered arrays with hundreds or thousands of alternating layers, with the thickness of individual layers in these arrays being in the order of nanometers. This process provides a rare opportunity to combine miscible polymers on a small scale with little or no mixing. Although the diffusion coefficients of the polymer chains are extremely low, in such systems with hundreds of layers diffusion can have a significant role [1, 2] and, thus, it is important to understand its kinetics and the mechanisms behind its development.

In this work we use co-extruded soft and hard thermoplastic urethanes as test materials to perform such a study both rheologically and by microscopy, looking especially at the influence of viscosity ratio on the development of interphases.

References: [1] E. Baer, J. Kerns, A. Hiltner, Structure Development during Polymer Processing, **370**, 327 (2000); [2] T. Schuman, S. Nazarenko, E. V. Stepanov, S. N. Magonov, A. Hiltner, E. Baer, Polymer, **40**, 7373 (1999).

Wednesday 5:30 Founders Ballroom PO78

The rheological footprint of the molecular structure of long-chain branched metallocene catalyzed polyethylenes

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Different rheological quantities, such as the zero shear-rate viscosity η_0 and the linear steady-state elastic compliance J_e^0 of long-chain branched metallocene-catalyzed ethene homopolymers and ethene-/a-olefin copolymers with a polydispersity M_w/M_n~2, were correlated with the molar mass M_w and degree of long-chain branching λ. A linear reference for the $\delta(|G^*|)$-plot was used to show the effect of long-chain branches on this rheological property. The linear steady-state elastic compliance J_e^0 correlated with the zero shear-rate viscosity increase factor η_0/η_0^{lin} and the characteristic phase angle δ_c. However, the latter only works when compensating for the influence of the molar mass on J_e^0 by the relationship between J_e^0 and M_w established elsewhere (Stadler and Münstedt, JoR, 2008). The characteristic phase angle δ_c and zero shear-rate viscosity enhancement factor η_0/η_0^{lin} are linked to each other by the linear dependencies for the type I and type II viscosity functions.

Wednesday 5:30 Founders Ballroom PO79

Dynamic-mechanical and adhesive properties of styrene-isoprene block copolymers blended with tackifier resin: Effects of macromolecular architecture

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Two different blends of styrene-isoprene-styrene (SIS) triblock and styrene-isoprene (SI) diblock copolymers with the same chemical composition but different molecular architecture have been investigated: a) linear SIS/linear SI b) star SIS/linear SI. These two samples were mixed with a hydrogenated resin by co-solvent casting. A set of copolymer/resin mixtures with varying resin content has been prepared and analyzed by means of DSC, probe tack debonding profiles and dynamic-mechanical tests. The linear viscoelastic behaviour of the copolymer/resin mixtures has been investigated by means of temperature sweep in oscillatory shear at a fixed angular frequency. Selected samples were analyzed also in terms of dynamic-mechanical spectroscopy in a wide range of frequencies in order to better elucidate the role of macromolecular architecture on short and long term rheological behaviour. Such characterization allowed optimizing the molecular architecture in view of the final applicative properties.

Wednesday 5:30 Founders Ballroom PO80

Viscoelastic catenaries

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Extensional flow of polymer melts is of major importance in a wide range of applications and processing technologies. In particular, complex extensional creep and recoil flows controlled by gravity and polymer elasticity are encountered in a number of practical situations typical of elastomer industry (e.g. cold flow during the storage period, sagging and shape distortions after extrusion of slender elastomer products). Understanding the sagging phenomenon induced by gravity on slender viscoelastic polymer samples, like filaments and thin films, is therefore not only a scientific challenge but also an important technological goal. Inspired by the experimental work by Roy et al. [J. Fluid Mech. (2006) 563, 283-292] on a viscoelastic Boger fluid, we investigated a set of entangled Polybutadiene samples with varying molecular architecture. Polymer samples were extruded in a Goettfert capillary rheometer in order to obtain filaments. The specimens were then allowed to relax for 24 hours in water bath in order to prevent shape distortion during this stage. Horizontal polymer filaments supported at both ends, have been stretched moving the supports apart. The filaments were then allowed sagging under the effect of gravity. After a certain sagging period, the supports were moved again to their original positions. In this way, the abrupt change of boundary conditions and filament shape originated an imbalance between elastic and gravity forces. The polymer filament started therefore rising driven by its elasticity. Different conditions of stretching ratio and sagging time have been used. The experimental results were compared with literature results and predictions regarding the sagging [Brochard-Wyart and De Gennes, EPL (2007) 80, 36001; Roy et al., J. Fluid Mech. (2006) 563, 283-292] and the rising stage [Roy et al., J. Fluid Mech. (2006) 563, 283-292].

Wednesday 5:30 Founders Ballroom PO81

X-ray scattering investigation of structural relaxation in an ordered block copolymer melt subjected to uniaxial extensional flow

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The structural dynamics of an ordered styrene-ethylene butylene-styrened triblock copolymer have been studied in uniaxial extensional flow using in situ x-ray scattering. Experiments were performed in a custom instrument consisting of an SER extensional flow fixture housed in a convection oven designed to facilitate x-ray access. Use of synchrotron radiation provided sufficient time resolution to study the structural response during inception of uniaxial flow, and as a function of time following flow cessation. The sample studied here exhibits hexagonally packed cylindrical microdomains of polystyrene embedded in a poly(ethylene butylene) matrix. Application of extensional flow produces multiple structural effects, including deformation of the microphase-separated morphology, and a complex reorientation process in which elongated PS microdomains progressively orient along the stretching axis. A series of experiments was run in which samples were stretching to varying Hencky strains, allowing investigation of the nature of structural relaxation from a variety of flow-induced structural states induced during extensional flow.

Wednesday 5:30 Founders Ballroom PO82

Droplet dynamics in a confined Poiseuille flow for polymer melts

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We examined droplet dynamics in a Poiseuille flow including the effect of a confinement by using PPM (polymer melt microfluidics). This type of flow can play an important role at the thin die section during extrusion or calendaring gap for immiscible blends and effect the final morphologies, eventually effecting bend properties. Nevertheless, droplet dynamics under high capillary number ($Ca > 10$) is not well studied in confinement. We utilize a flow focusing technique to form droplets which then travel down a downstream channel. Upon cessation of flow, we let the thread relax to droplets and then examine the dynamics upon re-initiation of flow. We show the droplet dynamics of three polymer pairs, polystyrene/polyamide (PS/PA), polystyrene/polyprophylene (PS/PP) and compatibilized pair PS/PP with styrene-ethylene-copylymer (SEP). The droplet shape varies according to the degree of confinement and positions across the channel depth in a Poiseuille flow. The shape shows the evolution from sphere to ellipsoid, bullet-like one and in a high confinement, parachute-like one at the center of channel depth as the degree of confinement increases. For the compatibilized pair (PP+SEP5%/PS), an unstable thread produces a wide distribution of droplet sizes (mostly small drops) upon cessation of flow, eventually turning to a series of small drops when the flow starts again due to the effect of compatibilizer. The thin thread breakup occurring on the long and thin tail ends of the droplet at high shear zone near channel walls is the main mechanism of drop generation in a high confinement Poiseuille flow.

Wednesday 5:30 Founders Ballroom PO83

New interfacial surface generator for the co-extrusion of micro- and nano-layered polymers

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Recent advances in layer-multiplying co-extrusion of incompatible polymers have made possible to fabricate multilayered nanostructures with improved barrier, thermal and mechanical behavior. However, existing layering techniques are very sensitive to mismatches in viscosity and elasticity of the co-extruded polymers which often give rise to layer non-uniformity and flow instabilities. In this work we present a new interfacial surface generator that markedly minimizes pressure drops and increases flow uniformity and compare its performance with the current design, both computationally and experimentally. The results show that not only is the resulting layered structure more uniform in the new die, the pressure drop is also down by up to 50%. Furthermore, the good agreement between simulations and experiments provides a blueprint for the design of multiplying dies tailored to the specific relative rheological characteristics of the co-extruded materials, thus widening the processing window and the range of materials that can be multilayered.

Wednesday 5:30 Founders Ballroom PO84

Improvement of hydrophilicity of polyethylene by cold plasma treatment

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In this study, the hydrophilicity of HDPE pellets was improved by low cold plasma treatment in a mixture of nitrogen and air plasma. Moreover, methyl methacrylate (MMA) monomer was added before the treatment in order to introduce the hydrophilic parts to the neat HDPE pellets compared to the samples which added an initiator (DCP). The change in hydrophilicity was analyzed by contact angle measurement. The value could be reduced from 96.8° prior to plasma treatment down to around 84.03° after treatment for 30 sec. The polar component of surface free energy of all samples were increased from the untreated HDPE from around zero to 11.92 mN/m indicating that MMA monomer and an initiator were successfully introduced the polar part to the HDPE. From SEM images, it can be seen that the roughness of all treated samples are higher than the neat HDPE sample, which is in accord to contact angle and surface free energy results. Furthermore, Ea for decomposition was increased after incorporating MMA from 300.34 kJ/mol for pure HDPE to 358.50 kJ/mol for MMA treated samples. Finally, the shear and extensional viscosities were studied to try to investigate the bulk properties of treated materials compared to the neat HDPE.

Wednesday 5:30 Founders Ballroom PO85

Study on flow induced nanoparticle orientation in polypropylene/organoclay nanocomposites films by means of rheological and birefringence techniques

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An attempt was made to study the role of matrix viscosity and nanoclay-matrix interaction on microstructure stability and/or organoclay reorientation. PP/PP-g-MAH/nanoclay (PP based) and PP-g-MAH/nanoclay (PP-g-MAH based) nanocomposite samples contains the same amount nanoclay (cloisite 15A) loading (4%wt) prepared by the melt compounding and using a twin screw extruder at three draw ratio equipped with a slit die were considered. The results of rheological linear viscoelastic performed on the highly intercalated morphology of PP based samples showed a decrease in the low frequency storage modulus plateau value with increasing the draw ratio. However the results for PP-g-MAH based nanocomposites showed, in contrary to the PP based film; increasing draw ratio rate led to films with greater contribution of the 3D network evaluated in terms of increased low frequency range storage modulus. Furthermore the results of stress transient tests revealed an enhancement in the stress overshoot with increasing draw ratio for the PP-g-MAH based films while an opposite effect was observed for PP based nnocomposites suggesting a reduced contribution of the 3D network microstructure; the results were in good agreement with linear viscoelastic results. The results of hot stage polarized microscope performed on the PP based nanocomposites showed a distinct nanoclay-induced birefringence pattern at elevated temperature (180°C) whose value was found to be increased with increasing drawing ratio; while much weaker effect of orientation on birefrigence pattern was observed for PP-g-MAH based nanocomposites samples. These results suggest that the increased matrix nanoclay interaction and decreased viscosity of the matrix both are in the favor of accelerating of reorientation of the nanoclay flow induced orientation after the cessations of the flow.

Wednesday 5:30 Founders Ballroom PO86

Thermo-rheological behavior of BA-a and P-DDM benzoxazines

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Polymerization processes and influence of different temperatures of both BA-a and P-DDM based benzoxazines were characterized by Small Amplitude Oscillatory Shear (SAOS) in which two-steps polymerization mechanisms are found. Given the similarities in trends with the dynamic modulus and tand in both BA-a and P-DDM cure processes, it is likely that they have similar curing mechanisms. However, P-DDM cures at a much higher rate kinetically than BA-a does (two to four times faster in direct comparisons). This is most likely attributed to the different chemical makeup of the monomer's link between its two halves, which creates less molecular interference for P-DDM, and makes it easier for interaction between molecules to occur and therefore results in faster cure. Supplementing these theories is the comparison of tand trends, which shows two peaks at lower temperatures and one at elevated temperatures. The first low-temperature peak is theorized to be the ring-opening and small extent of propagation of the proposed reaction mechanism of benzoxazine, while the second peak is theorized to be the actual polymerization and buildup of a molecular network, and is much less outstanding in magnitude at higher temperatures.

Wednesday 5:30 Founders Ballroom PO87

Nonlinear rheology of high heat polycarbonate copolymer blends

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Automotive suppliers seek materials that can meet challenges such as higher temperatures from proximity to bulbs and thinner-wall parts for reduced mass. In this poster, we will discuss about the rheological performance of our high heat(Lexan XHT) polycarbonate(PC) copolymers compared to our competitor resin. In particular, the non-linear viscoelasticity of the copolymer blends was probed via Fourier transform rheology. A small amount of copolymer had a remarkable influence on the processing qualities of these blends

Wednesday 5:30 Founders Ballroom PO88

Non-linear parameter Q from FT-rheology under LAOS flow for polymer composite systems

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Large Amplitude Oscillatory Shear (LAOS) is a test method for the characterization of complex fluids. Among several LAOS analysis methods, the Fourier Transform (FT)-Rheology is sensitive method. We proposed a new nonlinear coefficient Q established from FT-Rheolgy under LAOS. The parameter Q is defined as $Q = I_{3/1}/\gamma_0^2$ where $I_{3/1}$ is the normalized 3rd harmonic contribution. Asymptotic value zero-strain nonlinearity, Q0, the inherent non-linearity for vanishing strains can be defined. Using this concept entangled linear monodisperse polymer and comb polymer melts were investigated towards these nonlinear parameters (Q and Q0). A strong influence of the molecular topology on these nonlinear parameters (Q and Q0) was found. In this study, we also applied Q and Q0 to study polymer composite systems. We have investigated nonlinear and linear viscoelastic response under dynamic oscillatory shear flow for polymer composite system with various shapes of nanocomposite, e.g. PCL/MWNT (multiwall carbon nanotube, tube shape), PCL/ OMMT (orgnomodified montmorillonite, plate shape with high aspect ratio) and PCL/PCC (precipitated carcium carbonate, cubic shape). For better comparison of polymer composite system, we propose new parameter as the Nonlinear-Linear viscoelastic Ratio (NLR) as a function of composite concentration. In case of NLR>1, nonlinear parameter (Q0) can amplify more information of internal structure than linear parameter (G*). In case of NLR<1, nonlinear parameter amplify less than linear parameter. From the results, NLR is roughly calculated for various polymer composite systems, i.e. NLR(PCL/OMMT) ˜ 2205 > NLR (PCL/MWNT) ˜ 934 > NLR (PCL/PCC) ˜ 1.46 > NLR =1 > NLR (PVA/Borax) ˜ 0.18. It can be inferred that more dispersed system has larger NLR value. From these results, nonlinear parameter Q can be useful for investigating polymer composite system as well as polymer melt system.

Wednesday 5:30 Founders Ballroom PO89

Measurement of rheological properties of polymer solution using dynamic light scattering (DLS) and diffusing wave spectroscopy (DWS) methods

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The rheological analysis of particulate polymer solution systems is one of significant research subjects due to their industrial importance. The rheological properties of suspensions can be measured through various rheological tests. DLS and DWS methods using scattered light signals from the sample have been incorporated in this study to estimate its viscoelastic properties. In two methods, free motions of some probe particles suspended in the solution lead to the fluctuation of light signal for generating intensity correlation function. From the correlation functions, mean square displacement (MSD) of probe particles is directly calculated at very short time scale so the viscoelastic properties can be measured in the high frequency regime beyond the measurement range of conventional rheometers. Properties measured by DWS which is strongly dependent on the cell geometry and scattering mode have been compared with those by DLS and conventional rheometers.

Wednesday 5:30 Founders Ballroom PO90

Two methods of coarse-graining solvent-polymer interactions in bead spring chains

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Solvent interactions of long polymer molecules can significantly affect the dilute solution rheology. These interactions are a balance between attractive and repulsive contributions. We have developed two new methods to account for these interactions in bead-spring chain models. In the first method, we have coarse grained solvent mediated repulsive interactions between polymer segments by means of a new spring force law. We find that some molecules do not undergo a coil-stretch transition in extensional flows. This method cannot account for attractive interactions between different segments of the polymer chain. Therefore, we have developed a second method in which we account for both attractive and repulsive interactions and study the effect of rotation and elongation in formation of structures in flow.

Wednesday 5:30 Founders Ballroom PO91

Decay of elastic turbulence in a von Karman swirling flow

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An experimental study of the decay of Elastic Turbulence in a von Karman swirling flow of a dilute polymer solution is presented. Various decay regimes are characterized by combined measurements of the integral power injected into the system and local measurements of the velocity gradients as a function of the initial Weissenberg number. A detailed description of the time evolution of the decaying flow structures is presented. The characteristic decay time scales of the locally measured velocity gradients in both the bulk and in the elastic boundary layer of the flow are compared to the characteristic decay times of the integral power, the Eulerian correlation time of velocity fields and the largest relaxation time of the polymer solution. Based on these results, the possibility of exciting transient or spatiel localized nonlinear states is explored.

Wednesday 5:30 Founders Ballroom PO92

Effect of extensional properties on air-blast atomization for very dilute polymeric solutions

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Air-blast atomization of complex fluids is a key process in many industrial applications. After atomization, dilute polymeric solutions with similar, low values of high shear-rate viscosity (HSV) often exhibit different values of Sauter Mean Diameter (SMD) in their spray size distributions as a result of differing extensional rheological properties. In this work, we explore the atomization of Polyethylene Oxide (PEO) solutions dissolved in water/glycerol. Each solution is sprayed with an air-blast spray gun (SATA ®) at similar conditions and imaged with a LaVison® spray measurement system. The values of HSV for each solution are close (within 15%) to the solvent viscosity (3.22 mPa.s) and the variations in surface tension are negligible. However both the SMD and the size distributions change considerably between samples. For the highest molecular weight systems, interconnected beads-on-string structures are observed at different positions of the spray fan. These differences are due to differing elongational properties; but quantifying the extensional rheology of low viscosity dilute solutions is a well-known challenge. Capillary Break-up Extensional Rheometry (CABER) can be used for extensional rheometry of the more viscous solutions, but well-known limitations of this approach include inertially-induced asymmetries, gravitational sagging, beads-on-string formation, and very short break-up times, and this limits the range of relaxation times that can be probed. Consequently we also explore the use of jet break-up rheometry in complex fluids at realistic timescales and deformation rates. The jet is excited by a piezo-actuator at a known frequency as it exits a nozzle, and stroboscopic imaging using a commercial system (JetXpert ®) enables high temporal and spatial resolution. Analyzing the evolution in the jet diameter before break-up gives meaningful values of relaxation times that can be correlated with the differences in spray size distributions and the SMD values.

Wednesday 5:30 Founders Ballroom PO93

X-ray photon correlation spectroscopy during homogenous shear flow

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X-ray photon correlation spectroscopy (XPCS) allows studies of structural dynamics in a wide range of soft materials. It is naturally suited for probing length scales ranging from tens to hundreds of nanometers, and time scales ranging from milliseconds to hundreds of seconds. This range of scales is similar to that which governs (and is manifested in) the structural and rheological response of many complex fluids subjected to shear flow. This raises the question of whether XPCS may be extended to study changes in micoscopic dynamic processes induced by flow by performing XPCS measurements during application of shear flow. Extraction of information about flow-induced changes to a sample's dynamics will be complicated by the fact that the deterministic motion of fluid microsctructure associated with the imposed velocity gradient will greatly accelerate relaxation of the intensity autocorrelation function measured in XPCS throughout most of reciprocal space. This poster presents experiments that demonstrate the feasibility of performing XPCS in a linear shear flow, and that confirm theoretical predictions of the impact of shear on the autocorrelation function.

Wednesday 5:30 Founders Ballroom PO94

Slotted plate device to measure the yield stress of biofluids

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The slotted plate device is redesigned for low yield stress measurements, especially for studying complex biological fluids. Compared to the original device (Zhu, et al. 2001), the newly built apparatus improves the force measurement with a balance of fine resolution and smoothes the

vertical motion with a lab jack. The slotted plate geometry is being optimized via Computational Fluid Dynamics (CFD), to further reduce wall slip as well as pressure drag force. To improve the yield stress measurement accuracy, the proposed design has a large slot area ratio, a large number of slots as well as sharp front and rear edges. A theoretical model is proposed to describe the thixotropic behavior of yield stress fluids. So far, model predictions show satisfactory agreement with rheological experimental data for a dilute Carbopol solution under steady state conditions.

Wednesday 5:30 Founders Ballroom PO95

Non-Newtonian displacement flow in a Hele-Shaw cell

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A numerical and experimental investigation of the displacement of a Newtonian liguid by a non-Newtonian one in a rectangular Hele-Shaw cell was carried out. The Saffman-Taylor or viscous fingering instability occurs at the interface when one fluid pushes a more viscous one, and a Hele-Shaw cell is a convenient tool to observe this phenomenon. Applications include displacement of heavy crude oils in reservoirs, drilling fluid invasion of porous media, fracture conductivity, polymer processing, hydrology, and filtration. The Saffman-Taylor instability in a Hele-Shaw cell has been extensively studied for Newtonian and non-Newtonian liquids displaced by air. However, displacement flows involving two liquids of comparable viscosity (nonzero viscosity ratio) have received very little attention. The construction details of a Hele-Shaw cell suitable for liquid-liquid displacement are given. The evolution of the interface shape was analyzed through a digital camera, as a function of the geometric, dynamic, and rheological parameters. From tracing the shape of the interface, the displacement efficiency was determined. Thus, the spectrum of situations in which there is formation of either fingers or "plugs" (flat interfaces) was determined for the displacement of a mineral oil by Xanthan gum. A fully 3-D numerical simulation of this displacement flow is also performed, using the finite volume technique and the Volume-of-Fluid method to solve the governing equations. There is no universal convention in the literature for presenting the results, so a novel set of dimensionless parameters is proposed, namely, a dimensionless flow rate, the rheological capillary number, and the behavior index of Xanthan gum. Among other findings, it was observed that, for a constant value of the behavior index and for a rheological capillary number of magnitude of 0,1, the displacement efficiency increases with the dimensionless flow rate, because the viscosity ratio decreases.

Wednesday 5:30 Founders Ballroom PO96

Investigation of UV-induced and thermal curing reactions by simultaneous rheometry and FT-IR

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The use of UV curing materials has been widely utilized in many industries for processing or application of paints, inks, adhesives, coatings, etc. This technology combines environmental and economical advantages with improved product features. A curing process can be monitored by dynamic rheological measurements, since the build-up of a network in the sample is directly related to the change of the viscoelastic properties (G', G", etc.) of the material. By combining oscillatory rheological measurement with a second analytical technique an even more comprehensive insight into the characteristics of curing processes can be achieved. Such a supplemental tool can be FT-IR spectroscopy. For a curing process or phase transitions in general, a rheometer can analyze the time dependent change of the viscoelastic properties of a material. However, the viscoelastic properties of a material depend on its structure and especially its structural changes during a curing process. Infrared spectroscopy is an excellent tool for determining structural changes on a molecular level. With the patented Rheonaut module, a standard FT-IR spectrometer is coupled to the Thermo Scientific HAAKE MARS rheometer to form one integrated system. To investigate UV curing materials with the Rheonaut module, a new fixture for the HAAKE MARS rheometer platform has been specially developed. This module consists of an upper shaft with an integrated mirror and an exchangeable quartz glass plate. There is also a holder for a collimator and light guide, which is mounted to the HAAKE MARS measuring head. This new setup enables the user to expose a material to UV-radiation while collecting rheological and spectroscopic data at the same time. It's the purpose of this poster to present technical details of the described setup and demonstrate the experimental results of the investigation of thermal and UV-curing processes. The presented data includes rheological as well as spectroscopic data.

Wednesday 5:30 Founders Ballroom PO97

Determination of the brittle-ductile transition temperature using a direct strain controlled DMA

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The tensile modulus and Tg (glass transition temperature) are important mechanical and thermal properties for thin film polymers. A typical DMA experiment designed to measure these material properties includes a ramp of temperature over a wide range while applying a sinusoidal strain at 1 hertz. The resulting stress response enables the calculation of storage modulus, loss modulus, tangent delta, and Tg. Another critical parameter to characterize thin film polymers, is the determination of the brittle-ductile transition temperature, Tb. This can be calculated from the elongation-at-break and elongation-at-yield curves. These results can ultimately be used to characterize the brittle fracture, yield behavior and rubber-like behavior as a function of temperature and time (rate of deformation).

Wednesday 5:30 Founders Ballroom PO98

The impact of thermal gradients in rheological measurements

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When performing rheological measurements there are many essential parameters which need to be taken into account in order to ensure an accurate rheological measurement. These parameters include control of the temperature as well as the applied shear stress or strain. It is widely understood that precise control of temperature is essential to obtaining reliable rheological data, due to great influence temperature has on most samples. However, inaccurate control of the sample temperature results in uncertainties and errors in many practical measurements still to this day. A variety of methods (active temperature control, gap control, temperature equilibration, and heating/cooling rates) were investigated to demonstrate their impact on rheological measurements.

Wednesday 5:30 Founders Ballroom PO99

Review, validation, and recommendations for concentric cylinder viscosity measurements

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The concentric cylinders (cup and bob) test geometry for rotational rheometers is important and widely used for both practical and fundamental reasons. Despite its importance and prevalence, some details of its operation are inadequately understood, in particular the accuracy of empirical correction factors used to account for "end effects" from liquid outside the annular region of principle deformation, below and sometimes above the bob. We review standard operating procedures for concentric cylinder viscosity measurements, and explore these end effect sources of error and variability. Commonly-made corrections are checked for accuracy, and recommendations are made for practical operation. The conical end (DIN standard), the recessed end, and the double gap geometries are examined with Newtonian liquids of viscosities from 1-500 mPa.s and two surface tension values.

Wednesday 5:30 Founders Ballroom PO100

Optical encoder enhancements for better rheological measurements

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Optical encoders measure extremely small displacements, because no system is infinitely stiff, the slightest movement in the direction away from the reader limits absolute measurable resolution and leads to more noise (error) in phase and displacement, and is subject to drift over time. Magnitude and direction of drift will depend on many factors including temperature, deformation conditions, torque and normal force, sample, environment, etc. Enhancements in the optical encoder technology have been studied to limit these Issues which will lead to better rheological measurements. Measurements done at very low shear rates and oscillation measurements at low strains have been studied

Wednesday 5:30 Founders Ballroom PO101

Importance of true rate and strain for rheological testing

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Increased popularity of rheological measurements in the non-linear flow regime has brought attention to questions regarding the control of applied strain to the sample and accuracy of measured sample stress. The Combined Motor transducer rotational rheometer using air bearing-supported electrically commutated synchronous motor (EC motor) offers both stress and strain/strain rate control in rotation as well as in small amplitude oscillatory shear (SAOS) flow.

TruStrain^{TM} enables real time position control for setting an ideal-sinusoidal strain waveform by adapting itself to the theoretical sinusoidal waveform. TruStrain^{TM} capabilities are essential to large amplitude oscillatory shear (LAOS) as the sample might react differently on sinusoidal strain compared to sinusoidal stress input. Besides the sinusoidal strain setting TruStrain^{TM} allows to measure down lowest torques in oscillatory mode.

The advent of control mechanisms in rotational tests has enabled faster and more accurate control of sample strains and strain rates. The new adaptive controller TruRate^{TM} gives this rheometer an edge over competing controllers as its performance is almost independent of the measuring system used and does not require any pre-information about the sample to control the desired settings accurately.

Wednesday 5:30 Founders Ballroom PO102

A new method to evaluate dynamic data near T_g

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In this work, we compare and analyze the glassy modulus obtained by the KWW[1] and the BSW[2] functions for small molecule,[3] polymer[4] and colloidal glass formers[5] in the context of the Dyre shoving model.[6] The Dyre shoving model relates the glassy modulus with temperature by attributing the free-energy barrier for a "flow event" near to the glass transition temperature T_g to the work done by shoving aside the surrounding molecules; the free-energy barrier is proportional to the glassy modulus, which increases as the temperature decreases. Importantly, the model gives a non-singular growth of the relaxation time or viscosity with decreasing temperature and does not invoke ideas related to dynamic heterogeneity and growing length scales, both of which are commonly used in the description of glassy dynamics. To the extent that the material classes investigated seem to be reasonably described by the shoving model, it is suggested that divergence of time scales and length scales may not be essential to the glass transition phenomenon.

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Wednesday 5:30 Founders Ballroom PO103

Rheological analysis under pressure

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Typical rheological tests are all performed under atmospheric pressure conditions. However, in certain applications such as oil drilling, people need to evaluate the visco-elastic properties of materials under high temperature as well as high pressures. In addition, to evaluate high temperature viscosity of some volatile solutions, one will need a sealed vessel to prevent evaporation and also to hold the sample higher than the atmospheric pressure. In this paper, we introduced a pressure cell unit, which is used on TA Instruments AR series rheometers. This pressure cell accessory is capable of measuring the visco-elastic properties of samples up to 150°C with a pressure as high as 2000psi (138 bar). This accessory can be a very helpful tool for industries such as oil drilling, food, petroleum or pharmaceuticals that need high temperature and high pressure rheological measurements.

Wednesday 5:30 Founders Ballroom PO104

A lubricated cross-slot channel with 2D complex flow kinematics as an optical rheometer for polymer melts

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A lubricated cross-slot channel rheometer producing strong extensional deformation in the stagnation region is a unique device to study the viscoelastic behavior of polymer melts in a 2D complex flow situation. Moreover, it provides a valuable possibility to assess the performance of constitutive equations in predicting the stress field in mixed flows. In this work, the device capability is demonstrated on two polyethylene melts possessing a linear and highly branched structure, respectively. The stress field is captured non-invasively using point-wise and field wise birefringence techniques and the 2D kinematics of the complex flow is acquired employing particle tracking velocimetry. Furthermore, the eXtended Pom-Pom (XPP) model is solved using the regularized experimental flow kinematics through integration over streamlines. This approach allows the non-linear parameters of the constitutive equation to be optimized by fitting directly the point-wise flow induced optical signals collected from the mixed flow. Results show that the presence of long chain branches in the polymer structure generates high stress values near the outflow centerline influencing both the flow kinematics and the birefringence pattern. Furthermore, the theoretical principal stress difference (PSD) calculated for the long chain branched polyethylene using the XPP model exhibits extra fringes close to the inflow channel walls, which are seen neither in the point-wise nor in the field-wise flow induced birefringence experimental patterns. This discrepancy is explored by comparing the steady state first normal stress difference coefficient (Ψ1) obtained from the experimental optical signals in the fully developed part of the flow and from step shear rate measurements. Results suggest that Ψ1 for the highly branched polyethylene is not attainable by common shear rheometry measurements and is systematically over-predicted by the constitutive model, although the steady state shear viscosity (η) is correctly estimated.

Wednesday 5:30 Founders Ballroom PO105

Linear and nonlinear rheology and morphology of LCST blends with high viscosity ratio

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We investigated the correlation between the time evolution of the different phase-separating morphologies and corresponding linear rheological behavior as well as stress growth response upon start-up of shear flow for the dynamically asymmetric PS/PVME blend in which there is a large difference between glass transitions of the pure components (about 125 oC). The phase diagram was obtained from dynamic temperature sweep experiments. Phase contrast optical microscopy was employed to investigate morphological evolution of PS/PVME blends at various regions of obtained phase diagram at a constant temperature of 105 oC. At this temperature depending on sample composition, the viscoelastic phase separation (VPS) was observed besides the usual phase separation mechanisms (nucleation and growth (NG) and spinodal decomposition (SD)), indicating the interplay between thermodynamics and viscoelasticity in phase-separation behavior of PS/PVME blends. The linear viscoelastic behavior for different phase separating mechanisms (NG, SD, and VPS) was measured to investigate the kinetics of phase separation. It was found that the linear viscoelastic behavior can be described by Palierne's emulsion model, if the self-generated stresses induced during the phase separation in the matrix phase are taken into account. Furthermore, the stress growth behavior of different phase-separating morphologies was investigated by transient start-up of shear flow. To the best of our knowledge, there is no study on the rheological behavior of phase-separating blends under VPS (viscoelastic phase separation mechanism and its comparison with SD (spinodal decomposition) and NG (nucleation and growth) ones in the literature.

Wednesday 5:30 Founders Ballroom PO106

Ternary additives affect the gelation behavior and structural evolution of PEO-PPO-PEO gels as measured by rheology, DSC, and time-resolved SAXS

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Aqueous solutions of polyoxyethylene-polyoxypropylene-polyoxyethylene (PEO-PPO-PEO) triblock copolymers (commercially available as Pluronic® surfactants) undergo micellization and structural arrangement into cubic quasicrystalline lattices as their temperature is raised. This reverse-thermal gelation property has made Pluronic® F127 a material of interest for controlled release applications. We have investigated the effects of added methylparaben (MP) and dexamethasone (DX) on the kinetics of F127 gelation using rheology and DSC. Additionally, we have studied changes in the structural evolution as a result of these added constituents using time-resolved SAXS. Adding MP results in lowered gelation temperatures and faster gelation times as compared to neat F127, and a dependence on heating rate is also evident. Structural evaluation of these solutions confirms enhanced micelle ordering in the presence of MP and DX, allowing gels to form at lower temperatures and persevere at higher temperatures. Additionally, added MP affects the structural evolution mechanism in F127 solutions, causing a change from heterogeneous to homogeneous nucleation and growth. Finally, we made several interesting observations throughout the course of these studies. We found that added MP greatly suppresses the micellization endotherm in F127 solutions. SAXS measurements of these MP-containing solutions, however, confirm that micelles still form and organize. Added DX produces a unique scattering behavior where the primary scattering peak associated with the quasicrystalline structure is absent at low to medium temperatures, but becomes visible at high temperatures. These unusual observations shed light on the specifics of the molecular interactions that take place in amphiphilic copolymer systems with ternary constituents.

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Plenary Lectures and Award Presentation

Monday, October 10 *8:30 AM, Amphitheater A/B*	**Directed assembly of complex fluids, and its application to nanoscale fabrication** Juan J. de Pablo *Department of Chemical and Biological Engineering, University of Wisconsin-Madison*
Tuesday, October 11 *Bingham Lecture* *8:30 AM, Amphitheater A/B*	**The local and non-local rheology of vesicle and capsule suspensions** Eric S. Shaqfeh *Chemical Engineering, Mechanical Engineering, ICME, Stanford University*
Wednesday, October 12 *8:30 AM, Amphitheater A/B*	**Reversibility, rheology, and nonequilibrium phase transitions in periodically sheared suspensions of non-Brownian spheres and rods** David J. Pine *Department of Physics, New York University*
Thursday, October 13 *Metzner Awd. Presentation* *8:00 AM, Amphitheater B*	**Modelling flow-induced nucleation in polymers** Richard S. Graham *School of Mathematical Sciences, University of Nottingham*

Social Program

Sunday, October 9	**Welcoming Reception** 7:00 PM – 9:00 PM	 Founders Ballroom
	Sponsored by a generous contribution from TA Instruments	
Monday, October 10	**Society Business Meeting** 12:15 PM	 Room 207
	Society Reception 6:30 PM – 9:00 PM	 Cleveland Museum of Natural History
	Sponsored by a generous contribution from Malvern Instruments	
Tuesday, October 11	**Awards Reception** 7:00 PM – 8:00 PM	 Terrace Club Pub, Progressive Field
	Sponsored by a generous contribution from Xpansion Instruments	
	Awards Banquet 8:00 PM	 Terrace Club, Progressive Field
Wednesday, October 12	**Poster Session Reception** 5:30 PM – 7:30 PM	 Founders Ballroom
	Sponsored by a generous contribution from Anton-Paar USA	

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