



# THE SOCIETY OF RHEOLOGY

## 76TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Lubbock Memorial Civic Center  
Lubbock, Texas  
February 13-17, 2005

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# Meeting Schedule

## Monday, February 14, 2005

8:30	G. H. McKinley (PL1)			
9:20	Coffee			
9:45	GP1	DS1	BS1	MF1
10:10	GP2	DS2	BS2	MF2
10:35	GP3	DS3	BS3	MF3
11:00	GP4	DS4	BS4	MF4
11:25	GP5	DS5	BS5	MF5
12:00	Society Luncheon			
1:50	GP6	DS6	BS6	MF6
2:15	GP7	DS7	BS7	MF7
2:40	GP8	DS8	BS8	MF8
3:05	GP9	DS9	BS9	MF9
3:30	Coffee			
3:55	GP10	SC1	BS10	MF10
4:20	GP11	SC2	BS11	MF11
4:45	GP12	SC3	BS12	MF12
5:10	GP13	SC4	BS13	MF13
5:35	End			
6:15	Society Reception			

## Tuesday, February 15, 2005

8:30	C. W. Macosko (PL2)			
9:20	Coffee			
9:45	GP14	SC5	EM1	MS1
10:10	GP15	SC6	EM2	MS2
10:35	GP16	SC7	EM3	MS3
11:00	GP17	SC8	EM4	MS4
11:25	GP18	SC9	EM5	MS5
11:50	Lunch			
1:50	GP19	SC10	EM6	MS6
2:15	GP20	SC11	EM7	MS7
2:40	GP21	SC12	EM8	MS8
3:05	GP22	SC13	EM9	
3:30	Coffee			
3:55	RM1	SC14	SA1	MS10
4:20	RM2	SC15	SA2	MS11
4:45	RM3	SC16	SA3	MS12
5:10		SC17	SA4	MS13
5:35	End			
5:40	Business Meeting			
6:45	Awards Reception			
8:00	Awards Banquet			

## Wednesday, February 16, 2005

8:30	D. Weitz (PL3)			
9:20	Coffee			
9:45	RM4	SC18	SA5	MS14
10:10	RM5	SC19	SA6	MS15
10:35	RM6	SC20	SA7	MS16
11:00	RM7	SC21	SA8	MS17
11:25	RM8	SC22	SA9	MS18
11:50	Lunch			
1:50	RM9	SC23	SA10	MS19
2:15	RM10	SC24	SA11	MS20
2:40	RM11	SC25	SA12	MS21
3:05	RM12	SC26	SA13	MS22
3:30	Coffee			
3:55	RM13	SC27	SA14	MS23
4:20	RM14	SC28	SA15	MS24
4:45	RM15	SC29	SA16	MS25
5:10	RM16	SC30	SA17	MS26
5:35	End			
6:00	Poster Session & Refreshments			

## Thursday, February 17, 2005

8:05			EM10	MS27
8:30	FI1	SC31	EM11	MS28
8:55	FI2	SC32	EM12	MS29
9:20	FI3	SC33	EM13	MS30
9:45	Coffee			
10:10	FI4	SC34	EM14	MS31
10:35	FI5		EM15	MS32
11:00	FI6	SC36	EM16	MS33
11:25	FI7	SC37	EM17	MS34
11:50	End			

## Session Codes

BS = Biological Systems  
 DS = Dilute Solutions  
 EM = Experimental Methods  
 FI = Fluid Mechanics and Instability

GP = 50 Years of WLF: Glassy Polymers & Related Systems  
 MF = Multiphase Fluids  
 MS = Entangled Melts & Solutions

PL = Plenary Lectures  
 RM = Rheology at Microscopic Scale  
 SA = Self-Assembled & Associating Fluids  
 SC = Suspensions and Colloids

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# Monday Morning

## Symposium PL Plenary Lectures

Monday 8:30 Theater PL1

### **Stretched to breaking point: Measuring the transient extensional rheometry of complex fluids from the dilute solution to the melt**

Gareth H. McKinley

*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139*

Measuring the transient uniaxial extensional viscosity of non-Newtonian materials remains a challenge. The tensile stress growth is a function of both the rate of deformation and the total strain accumulated, and successful measurements require imposition of a deformation with constant stretch history. Experiments are further complicated by the vast dynamic range of forces and time scales that must be spanned. A number of instruments now enable the transient uniaxial extensional viscosity to be measured in a wide range of fluids. This talk will focus on development and operation of three such devices; (i) for very viscous materials such as polymer melts (with viscosities exceeding 1000 Pa.s) windup fixtures such as the SER provide an elegant means to measure the stress growth over a wide range of strains and strain rates and to probe mechanisms of sample failure; (ii) For 'mobile' liquids such as concentrated polymer solutions and Boger fluids that are viscous ( $\geq 1$  Pa.s) but not rigid enough to avoid sagging, Filament stretching extensional rheometers (FISER) provide one of the few ways of unambiguously measuring the transient tensile stress growth; finally (iii) for very dilute solutions and aqueous dispersions such as those used in inkjetting, drag reduction and in coating operations (with viscosities as low as 1 mPa.s) capillary breakup extensional rheometry (CABER) offers a way of measuring the transient elongational response. The connection between strain-hardening that develops during transient extension and the dynamical evolution in the profile of the samples towards their ultimate breakup is important in many industrial processing operations and is also manifested in heuristic concepts such as 'spinnability', 'tackiness' and 'stringiness'. Every-day examples include the spinning of ultra-thin filaments of silk by orb-weaving spiders, the stringiness of cheese and bread dough, the drying of liquid adhesives, splatter-resistance of paints and the unexpectedly long life-time of strands of saliva.

## Symposium GP 50 Years of WLF: Glassy Polymers & Related Systems

Organizers: Sindee Simon and Ed Quitevis

Monday 9:45 Room 104/105 GP1

### **Origins and subsequences**

Robert F. Landel

*Arefel Consulting, Santa Cruz, CA 95065*

WLF: How I was born and how I got my name, my footprints in the sands of time and some trolls which cling still to my frame.

Monday 10:10 Room 104/105

GP2

**Non-WLF behavior of the dynamics of glass-forming liquids in equilibrium but below the calorimetric glass temperature**

Gregory B. McKenna and Xiangfu Shi

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

While there is much data available concerning the temperature dependence and aging time dependence of the relaxation times for glasses that are not in equilibrium, presently there is limited data concerning the temperature dependence of the dynamics of glass-formers, including polymers, below the nominal glass temperature but in equilibrium. Data from O'Connell and McKenna [1] and from Simon and co-workers [2] indicate that some materials deviate away from the WLF extrapolation to fall on to a new Arrhenius behavior. On the other hand, Richert [3] has reported for dielectric measurements on PVAc that the sub-T<sub>g</sub> equilibrium response does reach the WLF extrapolation. Here we discuss the data and the implications of the departure from WLF behavior when it exists. We also provide new mechanical relaxation data for a sucrose benzoate glass-former that has been aged into equilibrium below the glass temperature. The temperature dependence of the shift factors are examined for departures from the WLF expectations.

[1] P.A. O'Connell and G.B. McKenna, *J.Chem. Phys.*,110, 11054-11060(1999). [2] S. L. Simon, J. W. Sobieski, and D. J. Plazek, *Polymer*, 42,2555-2567(2001). [3] R. Richert and H. Wagner,*Solid State Ionics*, 105, 167-173(1998).

Monday 10:35 Room 104/105

GP3

**Dielectric approach to viscous materials**

Ranko Richert

*Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604*

Dielectric relaxation techniques are routinely used in order to obtain detailed information on the dynamics of glassy and supercooled materials, like polymers, molecular liquids and other complex systems. While the mHz to GHz frequency range is standard, the equivalent of 20 nHz to 1.2 THz has been accomplished in terms of dielectric experiments. The enormous range and very high sensitivity result in a detailed picture on the dynamics for a wide range of materials. The temperature dependence of the average relaxation time will be analysed to demonstrate the existence of the typical break-points between different Vogel-Fulcher-Tammann (VFT) regimes and the transition from VFT to Arrhenius behavior.

The talk will also explore the technique of measuring the dielectric modulus by applying a charge at time zero and following the voltage across the sample as a function of time (while the amount of charge is kept constant). In this way, equilibrium relaxation times beyond 1 year have been recorded for poly(vinylacetate). This method is also advantageous for thermally stimulated approaches.

Monday 11:00 Room 104/105

GP4

**WLF, fragility, KWW analysis of mesoporous silica modified epoxies**

Nandika A. D'Souza<sup>1</sup>, Zhengtao Yang<sup>1</sup>, Decio Coutinho<sup>2</sup>, and Kenneth Balkus<sup>2</sup>

<sup>1</sup>*Materials Science and Engineering, University of North Texas, Denton, TX 75025;* <sup>2</sup>*University of North Texas, Denton, TX*

Mesoporous molecular sieves are of significant interest as particulate reinforcements of epoxy. Penetration of the particulate is possible due to the large pore architectures that may facilitate a physical bonding between the polymer and the particulate. Both as synthesized and porous particles were introduced into epoxies. Frequency-temperature measurements were conducted and mastercurves generated by horizontal shifting. The shift factor-temperature plots were analyzed using Arrhenius and WLF equations. A deviation from the C1 constant was observed in all mesopore modified epoxies. For small pores, C1 decreased with volume fraction whether the particle was porous or not. For large pores, C1 increased with volume fraction. C2 was found to be volume fraction independent. Following Angell's analysis on fragility, C1 was then set constant and C2 was fit. It was determined that the fragility of the epoxy increased with introduction of the particles. The fragility was however lower in the porous particles and dependent on pore size. The relaxation breadth analyzed by the KWW equation also reflected increased breadth of the transition.

Monday 11:25 Room 104/105

GP5

**Translational diffusion of probe molecules in supercooled liquids studied by holographic FRAP**Justin R. Rajian and Edward L. Quitevis*Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409*

A holographic fluorescence recovery after photobleaching (FRAP) technique has been used to measure the translational diffusion coefficient  $D_T$  of the probe molecule rubrene in supercooled liquids near the glass transition. Systems studied include rubrene in supercooled sucrose benzoate (SB) and supercooled *o*-terphenyl (OTP). The temperature dependence of  $D_T$  are compared with that of  $T/\eta$  in these liquids.

**Symposium DS  
Dilute Solutions**

Organizers: Graham M. Harrison and Matteo Pasquali

Monday 9:45 Room 107

DS1

**Characterization of the distribution of long chain branches in polyolefins**Patricia M. Cotts*CR&D, DuPont, Wilmington, DE 19880*

The characterization of long chain branches (LCB) in polyolefins and ethylene copolymers is a long-standing issue. Even very small amounts of long chain branching can have a large impact on processing and melt flow. Recent advances in on-line chromatography detectors including multi-angle light scattering, viscometry and FTIR have greatly advanced the opportunity to characterize the distribution of these branches. Recent theoretical work, as well as experimental work on model branched polymers (e.g. the pom-pom) has indicated that the placement as well as the length of these branches is critically important to predicting their impact on rheological properties. In this talk we present data on a wide variety of polyolefins. The degree of LCB is characterized by the reduction in polymer size relative to a linear polymer of the same molecular weight. Data is obtained using both light scattering and viscometric data on polymers fractionated on a high temperature chromatograph. Results from light scattering and viscometry are compared with each other and with theoretical models.

Monday 10:10 Room 107

DS2

**Critical crosslinking concentrations for guar and guar derivative solutions**Cuiyue Lei and Peter E. Clark*Department of Chemical and Biological Engineering, University of Alabama, Tuscaloosa, AL 35487*

Crosslinking of guar and guar derivatives is important in a number of industries. It is used extensively in the stimulation of oil and gas wells by hydraulic fracturing. For a number of technical and economic reasons, low polymer concentrations are desirable. Uniform crosslinked gels cannot be produced below some threshold concentration, and determining the concentration limit can be difficult and time consuming. A method of predicting the lower limit for the crosslinking concentration based on a easily measured fluid property is needed. The critical overlap concentration is a well-known property of dilute polymer solutions and is relatively easy to measure. There is some indication in the patent literature that low critical overlap concentrations are related to low crosslinking concentrations. We studied guar and guar derivatives, commonly used in oilfield applications to see if there was any relationship between the critical overlap and critical crosslinking concentrations. Five different polymers were examined (two different guar, hydroxypropyl guar, hydroxypropyl carboxymethyl guar, and carboxymethyl guar). The critical overlap concentration, intrinsic viscosity, Huggins coefficient, relaxation time, and  $\tan\theta$  as a function of frequency and concentration were measured or calculated. We took equations for critical crosslinking concentration and critical overlap concentration, both based on polymer molecular weight, and combined them to yield an equation that predicts the critical crosslinking concentration as a function of the critical overlap concentration. The equation predicts that a plot of critical crosslinking concentration versus critical overlap concentration should yield a

slope of 0.8. A plot of the experimental data yielded a slope of 0.78. It is interesting to note that the data appeared to be dependent on the polymer but not the type of crosslinker used.

Monday 10:35 Room 107

DS3

**Study of critical volume fraction and diffusion coefficients in nanotube/epoxy dispersion**

Krzysztof Koziol<sup>1</sup>, Sameer S. Rahatekar<sup>1</sup>, Simon Butler<sup>2</sup>, Malcolm Mackley<sup>2</sup>, and Alan H. Windle<sup>2</sup>

<sup>1</sup>*Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, United Kingdom;*

<sup>2</sup>*University of Cambridge, Cambridge CB2 3QZ, United Kingdom*

Highly aligned multi-walled carbon nanotube were dispersed in epoxy resin. The aim of the work is to find if there is a critical volume fraction above which nanotubes starts entangling. Samples of nanotube/epoxy dispersions were prepared with different volume fractions ranging from 0.1 to 1.5-wt percent. Rheological characterization such as finding viscosity,  $G'$  and  $G''$  was carried out using parallel plate rheometer at 25 C, 50 C and 80 C. The effect of shear force on degradation of nanotubes dispersed in epoxy is also studied as a function of shear rate and processing time. In the second set of experiments, the nanotube/epoxy dispersion was characterised using Multipass rheometer. The aim of second set of experiments is to determine diffusion coefficient of nanotube in dilute dispersion of nanotube/epoxy. The nanotube were aligned by shear-induced orientation using Multipass rheometer. Results obtained from the In situ x-ray diffraction measurements during relaxation of nanotubes would be presented.

Monday 11:00 Room 107

DS4

**Determining the distribution and average length of single-walled carbon nanotubes by viscosity measurements in dilute Brownian suspensions**

Nicholas G. Parra-Vasquez<sup>1</sup>, Ingrid Stepanek<sup>1</sup>, Virginia A. Davis<sup>1</sup>, Valerie C. Moore<sup>2</sup>, Erik H. Haroz<sup>2</sup>, Robert H. Hauge<sup>2</sup>, Richard E. Smalley<sup>2</sup>, and Matteo Pasquali<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Rice University, Houston, TX 77005;* <sup>2</sup>*Rice University, Houston, TX*

Determining the average length of a sample of single-walled carbon nanotubes (SWNTs) is becoming particularly important as the various methods for mass-producing SWNTs are being scaled-up and optimized, and as new methods are being developed for cutting SWNTs chemically and physically to prescribed length.

So far, length determination has relied chiefly on AFM measurements, which are time-consuming and suffer the drawbacks of small sample sizes and of possible errors induced by the sample preparation technique. Here we show that viscosity measurements in dilute solutions yield an average length of a macroscopic sample of SWNTs, and that the third moment of the length distribution calculated by using AFM measurements matches closely that measured directly by viscosity measurements on dilute SWNT dispersions.

Dilute SWNTs were dispersed either in sulfuric acid or in a solution of 2% wt. pluronic (PEO-PPO-PEO) surfactants. The zero-shear viscosity of each dispersion was measured with a strain-controlled rheometer. The difference between the viscosity of the dispersion and that of the solvent was found to be a linear function of concentration, as predicted by the Kirkwood-Auer theory for dilute Brownian rodlike particles. By using the Kirkwood-Auer relationship between zero-shear viscosity, rod diameter, and rod length corrected by Batchelor's formula for the drag on a slender cylinder, we find that the average length of the SWNTs ranges from 300 to 1500 nm depending on the reactor conditions. AFM measurements on functionalized SWNTs from the same batch are in excellent agreement with results obtained by viscosity measurements. Thus, we conclude that viscosity measurements in dilute solutions yield the average length of SWNTs (as they do in polymers); compared to AFM, they are simpler, less time-consuming, and less prone to errors induced by sample preparation. It seems possible to infer SWNT length distributions by using the whole viscosity curve.

Monday 11:25 Room 107

DS5

**Reduced-order modeling of dynamics of polymeric solutions under flow : A configuration-based approach**

Vidya Venkataramani, R. Sureshkumar, and Bamin Khomami

*Department of Chemical Engineering, Washington University in Saint Louis, Saint Louis, MO 63130*

Accurate flow simulations of dilute polymer solutions require the use of constitutive equations or micro-mechanical models that contain sufficient detail on microstructure evolution. However, as one moves from the realm of

qualitative continuum-level models to micro-mechanical descriptions with sufficiently large number of degrees of freedom, the computational complexity increases significantly. Consequently, self-consistent "micro-macro" simulations of multi-dimensional flows using realistic multi-segment models are computationally prohibitive. We present a computationally tractable, coarse graining approach based on the idea of "configuration sampling". In this approach, the configurational landscape of the polymer molecules is divided into a few ( $O(1)$ ) sub-domains, i.e., well-defined configurations such as folds, dumbbells, coils, extended and kinked states are identified via Brownian dynamics simulations (BDS) of steady and time-dependent homogeneous flows using multi-segment bead-spring models. BDS data are in turn used to develop a deterministic model for the evolution of the probability associated with finding a chain in a given configuration class. In addition, force laws of and contributions to the overall stress from the configuration classes are also modeled. The utility and accuracy of this model reduction approach for flow simulations of dilute polymeric solutions will be illustrated by an example namely, the stress-conformation hysteresis observed in strong extensional flows.

## Symposium BS Biological Systems

Organizers: Panos Dimitrakopoulos and Eric Furst

Monday 9:45 Room 108/109

BS1

### **Viscoelasticity of lung surfactant responding to environmental stress**

An Goffin<sup>1</sup>, Jay Anseth<sup>1</sup>, Gerald Fuller<sup>1</sup>, Daya Upadhyay<sup>2</sup>, and Peter Kao<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Stanford University, Stanford, CA 94305;* <sup>2</sup>*Department of Pulmonary and Critical Care Medicine, Stanford University, Stanford, CA 94305*

Residual oil fly ash (ROFA), an emission-source air pollutant, is known to induce acute lung injury and may cause surfactant damage. Using an Interfacial Stress Rheometer (ISR), which is a method that determines the rheology of fluid/fluid interfaces, and fluorescence microscopy; we demonstrate that ROFA-alveolar epithelial cell interaction induces lung surfactant gelation. Inhibitors of reactive oxygen species (ROS), a mitochondrial anion channel inhibitor, and A549  $\beta$  cells that lack mitochondrial DNA and functional electron transport block these effects to varying degrees; suggesting a role for both mitochondrial and non-mitochondrial ROS generation in epithelial cells in mediating ROFA-induced surfactant damage.

Monday 10:10 Room 108/109

BS2

### **Using single lipid tracking to investigate langmuir monolayer properties**

Martin J. Widenbrant and Gerald Fuller

*Chemical Engineering Department, Stanford University, Stanford, CA 94305-5025*

The dynamics of lipid monolayers are investigated using tethered fluorescent vesicles as probes. The vesicle is tethered to the monolayer using a "smart tether" consisting of complimentary ssDNA strands. This allows for direct measurements of the properties of the monolayer. A monolayer of lipids is spread, a fraction of these lipids carrying the ssDNA tether. Vesicles with the complementary ssDNA are injected into the subphase where they can diffuse to the interface and bind to the lipids. Once hybridized these are constrained to the 2D air water interface. The monolayer can consist of lipids independent of the vesicle composition; the monolayer can also have incorporated peptides and proteins. Images of the interface are recorded using a fluorescence microscope with an attached intensified CCD camera. The surface pressure is recorded at the same time. These images are analyzed and the diffusion coefficient at a certain surface pressure is noted. Initial experiments with incorporated peptides have been conducted.

The trend for the diffusion coefficient is that at higher surface pressure, less available area per molecule, the diffusion is hindered and yields a lower diffusion coefficient, than at lower surface pressures. Observations of vesicle interactions at the monolayer have been observed and will be reported.

Monday 10:35 Room 108/109

BS3

**Expression level of surface proteins under variable stress conditions**

Matthew B. Kerby and Anubhav Tripathi

*Division of Engineering, Brown University, Providence, RI 02912*

The study of biomolecular adhesion processes provides insight to cell-cell interactions via targeted ligand binding. Traditionally, these investigations are conducted using a straight channel flow cell with constant stress profile. In this work we have designed a Hele Shaw micro-geometry to study the binding mechanism of targeted cells. The flow provides a linearly variable shear to cells as liganded microspheres move under controlled binding conditions. Experiments were first performed using microspheres and coated surfaces to validate the flow and kinetic binding of ligands. A calibration curve was created to relate microsphere binding density to known densities of purified recombinant surface ligands. Subsequently, experiments were performed to quantify expression level of surface proteins under variable stress conditions using confluent cell lines. The coated channels were replaced by cells and, again using calibrated liganded microspheres, probed for the same surface molecules. Microsphere binding to the recombinant protein surface was inhibited under high shear conditions but, below a critical shear level, increased in an approximate stepwise fashion. The binding to the cells exhibited a different pattern since the expressed ligand surface density was also a function of applied stress. When corrected for surface density, the microsphere binding followed the same shear dependence found in the recombinant ligand microsphere system.

Monday 11:00 Room 108/109

BS4

**Flow around an endothelial cell attached to a micro-vessel wall**

Panagiotis Dimitrakopoulos and Yechun Wang

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Viscous flow over protuberances on the inner wall of cylindrical tubes has applications to industrial processes and physiological phenomena. In the latter case, the protuberances may represent attached leukocytes, separated endothelial cells or blood clots on the inner surface of capillaries or venules. Due to the comparable radius size of the micro-vessel and the endothelial cell, our study models the system as a three-dimensional cylindrical channel with a solid spherical cap attached to the inner tube surface while our Spectral Boundary Element method is employed. The force, torque and shear stress distribution on the cell are determined as a function of the contact angle and the size of the cell and the micro-vessel. The effects of the presence of leukocytes above the endothelial cell may also be presented.

Monday 11:25 Room 108/109

BS5

**The effect of magnitude and duration of shear exposure on the characteristics of red blood cell deformability**

Sung Sik Lee<sup>1</sup>, Nahn Ju Kim<sup>1</sup>, Kyung H. Ahn<sup>1</sup>, Seung J. Lee<sup>1</sup>, Kyung Sun<sup>2</sup>, James F. Antaki<sup>3</sup>, Marina V. Kameneva<sup>4</sup>, Johannes G. Dobbe<sup>5</sup>, and Max R. Hardeman<sup>5</sup>

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Red blood cells (RBCs) experience time-varying shear in vivo and in vitro. This study was undertaken to investigate the magnitude and the duration of shear exposure effect on the RBC characteristics in vivo and in vitro. We chose the degree of RBC deformation as a comparison criterion. To induce the deformation in rheologically well-defined flow, we designed the PDMS-glass hybridized micro channel and utilized the transparent parallel plates. Deformability was determined by optical measurement of the aspect ratio of the RBC images using an Automated Rheoscope Cell Analyzer (ARCA). A rotating Couette-type device was used to expose blood to elevated shear in vitro. Experiments were conducted wherein both the magnitude and exposure time were prescribed over a range of conditions from 16.9Pa to 112.8 Pa. The resulting measurements of deformability demonstrated an irreversible increase in stiffness with increasing shear exposure. These preliminary studies have motivated the investigation of mechanisms for shear-induced stiffening of RBCs.

## Symposium MF Multiphase Fluids

Organizers: Venkat Ganesan and Sachin Velenkar

Monday 9:45 Theater

MF1

### **Revision of some theories allowing determination of interfacial tension in polymer blends**

Mosto M. Bousmina

*Chemical Engineering, Laval University, Quebec, Quebec G1K7P4, Canada*

Revision of some theories allowing determination of interfacial tension in polymer blends Mosto Bousmina Department of chemical engineering, CREPEC, Laval University Ste-Foy G1K 7P4, Canada Canada Research Chair on Polymer Physics and Nanomaterials I. Introduction The interfacial tension plays a predominant role in multiphase systems, such as polymer blends and alloys. The properties of polymer blends are directly related to the properties of the components, to their morphology (distribution and dispersion of the phases), and to the properties of the interface/interphase. The interfacial tension is one of the essential parameters in characterizing and quantifying the interactions at such interface/interphase. Various techniques are available for the determination of the interfacial tension. The general principle of these techniques is based on a balance between a driving force (Brownian forces, gravitational and inertia forces, or viscous forces) and a resistance due to the interfacial force that tends to minimize the contact area between the phases. The breaking thread method (BTM) and the relaxation of a deformed droplet method (RDDM) are among the popular used techniques. The first technique is based on Tomotika's theory and the second one is based on small deformation theory. We give in this paper a detailed treatment of flow field at the interface in two-phase systems and we show that the use of both BTM and RDDM are only valid under very restricted conditions and maybe not suitable for the general case of polymer blends. Alternative theories will be exposed and will be compared with available experiments results.

Monday 10:10 Theater

MF2

### **Shear effects on rheology and phase behavior of polymer blends**

Bharad Narayanan, Victor Pryamitsyn, and Venkat Ganesan

*Chemical Engineering, The University of Texas at Austin, Austin, TX 78712*

We present the results of a multiscale simulation approach which combines Brownian dynamics simulations with polymer self-consistent field theory and continuum mechanics to study two effects: (i) The dynamical properties of polymer blend interfaces and the influence of block copolymer compatibilizers; (ii) The effect of externally applied simple shear flow on the phase behavior of polymer blends. In the first context, our numerical results agree quite well with the predictions from scaling approaches and phenomenological theories. Moreover, these results also provide a microscopic explanation of the negatively deviating viscosities of polymer blends. We also present results elucidating the "slip suppressing" influence of block compatibilizers. In the second context, we explore the effects of viscoelastic asymmetry and the composition dependence of polymer mobilities as driving forces for shear induced mixing and de-mixing phenomena seen in polymer blends. Our results suggest a rich variety of behavior arising from the interplay between viscoelasticity and thermodynamics and is in qualitative agreement with other theories and experimental observations.

Monday 10:35 Theater

MF3

### **Creep recovery of compatibilized blends**

Sachin Velankar and Jun Wang

*Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261*

Block copolymers are often employed to improve blending of immiscible homopolymers. This research is aimed at quantifying the rheological properties of such added block copolymers (dubbed "compatibilizers") on the rheological properties of blends. We will discuss creep recovery after cessation of shear in droplet-matrix blends with small amounts (< 1% by weight) of compatibilizer.

Blends were presheared at a high stress, then the stress was reduced, and recovery was measured as a function of shearing time at the lower stress. Droplets grew by coalescence after stepping down the shear stress, and the

Monday Morning

retardation time and ultimate recovery were found to increase with shearing time. In the absence of compatibilizer, recovery could be well-represented as a single retardation process. The ultimate recovery and retardation time were consistent with past experiments, and at least qualitatively consistent with past theory. With addition of compatibilizer, recovery could not longer be modeled as a single-retardation process. Moreover, the ultimate recovery increased significantly (by as much as 70%) with addition of small amounts of compatibilizer.

The results seem to be consistent with past numerical simulations of surfactant-laden drops in which gradients in compatibilizer concentration along the surface of drops enhance recovery. The results can also be modeled using past emulsion models by Oldroyd and by Paliarne. These models do indeed predict that interfacial viscoelasticity due to added compatibilizer can cause multiple retardation processes and increase the ultimate recovery.

Monday 11:00 Theater

MF4

### **The mesoscale structure of immiscible liquid-liquid systems during phase inversion**

Mark J. Biggs and Richard Layfield

*Institute for Materials and Processes, University of Edinburgh, Edinburgh, Mid-Lothian, Scotland EH9 3JL, United Kingdom*

Immiscible liquid-liquid dispersions occur across industry and beyond (e.g. oil-water flow in pipelines, liquid-liquid extraction, two-phase batch reactors, encapsulation). Phase inversion - the process whereby the dispersed phase becomes the continuous phase and vice versa - is often relevant in such systems. In some cases it is an essential element of the process (e.g. production of margarine), but in others it is undesirable such as in exothermic aromatic nitrations where phase inversion can cause a sudden increase in the reaction rate and consequently produced heat. Given the importance of phase inversion in immiscible liquid-liquid dispersions, it is surprising that the processes at the mesoscale are not well understood. A collaborative experimental and modelling study has therefore been undertaken by three groups from UK academia aimed at elucidating these processes; this presentation will report some of this work with an emphasis on the mesoscale modelling aspects.

Detail of the mesoscale model used, which is based on the Rothman-Keller immiscible lattice-gas automata algorithm modified to allow wide variation in the interfacial tension and viscosity ratio, will first be presented. Results for phase inversion in pipe flow will then be given and discussed. Results will include the evolution of the structure near and far downstream from a point of injection of liquid A into a dispersion of immiscible liquids A and B as a function of various process and fluid system parameters (e.g. velocity of the single liquid stream; viscosity ratio). The results will be in the form of graphical images, which will be compared directly with those obtained from LIF studies of index matched liquid-liquid dispersions, statistical measures of the fluid structure (e.g. cluster statistics) and changes in wall stresses.

Monday 11:25 Theater

MF5

### **Polymer mutual diffusion via rheology of multilayers**

Rui Zhao and Christopher W. Macosko

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

We have measured the mutual diffusion coefficient of HDPE/LLDPE using coextruded multilayers. Two polyethylenes with different molecular weight are coextruded into layer structure in about 45 seconds of contact time. When the multilayer sample is remelted in a parallel plate rheometer, its apparent viscosity increases due to the interdiffusion. By monitoring the kinetics of the apparent viscosity, the interdiffusion coefficient can be measured. This interdiffusion process is treated in two cases: assuming concentration independent interdiffusion coefficient and concentration dependent interdiffusion coefficient. In the first case, two interdiffusion coefficients have to be used to only fit the initial stage of the interdiffusion of the two multilayer samples with 30 and 50 vol% HDPE. In the second case, the theory of Kramer, et al. [Polymer 25:473, 1984], is used to describe the relation of the interdiffusion coefficient to the concentration. FEM is used to solve the nonlinear interdiffusion problem. One equation with same constants is used for the interdiffusion coefficient in the two multilayer samples, and the whole course of the interdiffusion can be fit. The range of the interdiffusion coefficient for these two PEs is found to be  $10^{-12} \sim 10^{-14} \text{ m}^2/\text{s}$  at  $200^\circ\text{C}$ . This work provides an easy and quick method to measure polymer interdiffusion coefficient.

# Monday Afternoon

## Symposium GP 50 Years of WLF: Glassy Polymers & Related Systems

Organizers: Sindee Simon and Ed Quitevis

Monday 1:50 Room 104/105

GP6

### **Disentangling density and temperature effects**

Christiane M. Alba-Simionesco<sup>1</sup>, Gilles Tarjus<sup>2</sup>, angel Alegria<sup>3</sup>, and Stefano Mossa<sup>4</sup>

<sup>1</sup>lab. Chimie Physique, C.N.R.S, Université Paris-Sud Orsay, Orsay, 91405 Orsay cedex 91405, France;

<sup>2</sup>CNRS, Paris, France; <sup>3</sup>Material science, Univ San Sebastian, San Sebastian, Spain; <sup>4</sup>ESRF, Grenoble, France

We try to provide a consistent picture of the respective role of density  $\rho$  and temperature  $T$  in the viscous slowing down of glassforming liquids and polymers at normal pressure, but also in a wide pressure and temperature range. Building upon our previous work and recent studies also done by others, including an analysis of simulation and experimental data on fragile, intermediate liquids and polymer melts, we conclude that, although density plays a role at a quantitative level in the viscous slowing down of glassformers, its effect can be scaled out by introducing an effective energy  $E \propto (\rho)$  characteristic of the high-temperature liquid regime. For polymers, when high temperature data are not available, we show that the density and temperature dependences of the segmental relaxation time can be described through a single scaling variable  $X = e(\rho)/T$ , where  $e(\rho)$  is well fitted by a power law  $\rho^x$  or by a one-parameter linear description  $e(\rho) = \rho - \rho^*$ ,  $x$  and  $\rho^*$  being species-specific parameters. This implies that "fragility" is an intrinsic, density-independent property of a glassformer characterizing its super-Arrhenius slowing down of relaxations. A zeroth-order description of the viscous slowing down of liquids and polymers as one approaches the glass transition should thus be formulated in terms of a temperature-driven super-Arrhenius activated behavior rather than a density-driven congestion or jamming phenomenon. We discuss the consequences of this analysis on the WLF formulation.

Monday 2:15 Room 104/105

GP7

### **Scaling of the segmental relaxation times of polymers**

C M. Roland and Riccardo Casalini

Code 6120, Naval Research Laboratory, Washington, D.C. 20375-5342

From analysis of a wide range of isothermal and isobaric data, we find that the segmental relaxation times of a polymer measured at various temperatures and pressures can be superposed by expressing them as a function of temperature times the specific volume raised to a power. The scaling exponent is a material-specific constant, which can be linked to the nature of the intermolecular repulsive potential for the material. Thus, the value of the exponent reflects the relative contributions of thermal energy and density to the temperature dependence of the local dynamics. From the scaling relation, we derive the Boyer-Spencer and Bondi empirical rules, concerning the product of the thermal expansion coefficient and the glass temperature. The scaling can be extended to the global dynamics of polymers, using a value of the exponent identical to that for local segmental relaxation. This equivalence of the scaling exponent is consistent with one of the central tenets of the Rouse and reptation descriptions of the low frequency dynamics of chain molecules.

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Monday 2:40 Room 104/105

GP8

**The relationship between polymer mobility and potential energy**

Douglas B. Adolf<sup>1</sup>, Joanne Budzien<sup>2</sup>, and John McCoy<sup>2</sup>

<sup>1</sup>Materials and Process Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185;

<sup>2</sup>Materials and Metallurgical Engineering, New Mexico Tech, Socorro, NM 87801

The WLF equation is typically used to describe the dependence of polymer mobility on temperature at atmospheric pressure. Tests at different pressures would at least require different WLF parameterization. Completely different tests, for example, probing the temperature dependence of mobility at constant density, would require even greater modifications. By performing molecular dynamics simulations on simple chain molecules equilibrated at different thermodynamic states, we have shown that the mobility depends in a more general sense on the potential energy density of the system. That is, mobilities for any equilibrated state collapse onto one master curve when plotted against the potential energy density. Moreover, this relationship can be fit by either a "generalized" WLF equation or by a power-law relationship observed in critical phenomena. When this mobility relationship is used within a rheologically simple, thermodynamically consistent, viscoelastic framework, quantitative agreement is seen between experimental data and theoretical predictions on a range of tests covering enthalpy relaxation to mechanical yield to physical aging.

Monday 3:05 Room 104/105

GP9

**Are rate processes of amorphous materials determined by the fractional free volume?**

Donald J. Plazek

*Dept. of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261*

As an observer of the birth of the Williams, Landel and Ferry Equation we will give an informal personal depiction of the events surrounding the development of the relation. Since Williams, Landel and Ferry showed with the fractional free volume,  $f = v_f / v$ , varying linearly with temperature, their equation for the relative temperature variation of the relaxation or retardation times was equivalent to or derivable from the Doolittle equation of the viscosity.  $v_f$  is the free volume and  $v$  is the volume. This equivalence infers that the rates of kinetic processes in amorphous materials between  $T_g$  and  $T_g + 100^\circ\text{C}$  is determined by the relative or fractional free volume. This conclusion has been questioned and often denied. This controversy will be discussed.

Monday 3:55 Room 104/105

GP10

**WLF/VFT equation look-alikes, with thermodynamic accounts of the fragility, inside**

C. Austen Angell

*Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85297*

The WLF equation is one of the enduring equations of polymer relaxation physics. In this talk we provide some insight into the source of its durability by transforming it twice, at each transformation breathing new life into its otherwise barren C1 and C2 parameters. Part of its durability is attributable to the attention that WLF first attracted by virtue of the apparent "universality" of its parameters. In particular the parameter C1 tended to have a fixed value of 16 when the reference temperature was chosen to be the glass temperature (where  $t(T_g) = 100\text{s}$ ) and the range of data was large. We put physics into this universality by showing, via a transformation to the equally enduring Vogel Fulcher Tammann VFT equation ( $\tau = \tau_0 \exp(B/[T-T_0])$ ), that C1 is 16 because, at the limit of high temperature, all liquids and polymers relax on the same short time scale  $\tau_0$  which is the vibration time for the molecule (bead, or chain unit),  $10^{-13.5}$  sec. This leaves C2, which has proven to be far less universal, as the carrier of information on the fragility of the liquid that in the VFT equation, is contained in the ratio  $B/T_0$ . In the second transformation, we show how the fragility itself is determined by a single parameter  $s^*$ .  $s^*$  is the entropy change per molecule (bead or chain unit) involved in the fundamental configurational excitation process for the amorphous system, (the equivalent of the formation of a defect in a crystal, but Gaussian in energy distribution and complex in topology). In the case of liquids (but not polymers) it determines both the thermodynamic and kinetic fragilities. Via this transformation, the WLF equation is seen to be a transcendental function of the elementary configurational excitation parameters of the glass.

Monday 4:20 Room 104/105

GP11

**The WLF temperature and volume dependences of molecular mobility in glass-forming substances originates from the secondary Johari-Goldstein relaxation**Kia L. Ngai*ESTD, Naval Research Laboratory, Washington, D.C. 20375-5320*

Broadband dielectric relaxation data of many glass-forming substances at atmospheric and elevated pressures are used to show that, in the equilibrium liquid state, the secondary Johari-Goldstein (JG) relaxation time has the WLF temperature dependence and is strongly pressure dependent. From these experimental results, we conclude that the dependence of molecular mobility on volume, entropy and temperature has already entered into the JG relaxation long before the primary relaxation becomes known. Thus a theory of glass transition needs reconsideration if the primary relaxation is considered as where the dependence of molecular mobility on temperature, volume and entropy originates. We present evidences that many-molecule dynamics must be taken into account in considering the primary relaxation. The many-molecule dynamics transform the precursory and local JG relaxation to the primary relaxation, resulting in the latter being dynamically heterogenous over a larger length-scale. The observed stronger dependence of the primary relaxation time on temperature, volume and entropy is the consequence of the many molecule dynamics, through which the originating weaker dependence of the JG relaxation time is amplified. The experimental results are discussed in terms of the coupling model of the author, which starts from the primitive (independent) relaxation and arrives at the primary relaxation after considering the effects of many molecule dynamics on the former, causing it to be dynamically heterogenous and slowed down. The length-scale of the heterogeneous dynamic is thus proportional to the coupling parameter, in agreement with experiment. The primitive relaxation time is approximately the same as the JG relaxation time, a remarkable finding that gives support to the coupling model.

Monday 4:45 Room 104/105

GP12

**Nanothermodynamics and the Williams-Landel-Ferry equation**Ralph V. Chamberlin*Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504*

The WLF equation has been extraordinarily successful at characterizing the non-Arrhenius behavior of materials; but there is still no fully accepted physical basis for the formula. Two key features in the WLF equation are: the sharply divergent response times, and the relatively constant spectral width (time-temperature superposition). It is remarkable that this "universal" dynamics occurs in such a wide variety of complex materials, especially since it is now known that the dynamics often involves heterogeneity on the scale of nanometers. We are developing a novel approach towards understanding the WLF formula based on small-system thermodynamics. Although this "nanothermodynamics" was originally intended to describe the thermal properties of isolated small systems, we have extended the ideas to consider independent thermal fluctuations inside bulk materials. We will present evidence from measurements, theory, and simulations showing that the non-Arrhenius response of many complex materials involves nanothermodynamics.

Monday 5:10 Room 104/105

GP13

**Local energy exchange model for predicting super-Arrhenian behavior**Grigori A. Medvedev and James M. Caruthers*School of Chemical Engineering, Purdue University, West Lafayette, IN 47907-2050*

One of the key signatures of a glassy material is the strongly non Arrhenian temperature dependence of the relaxation response, which is empirically described by the well known WLF equation. Numerous models (i.e. free volume, configurational entropy, etc.) have been proposed to explain the origin of the WLF equation; however, these models do not provide a direct connection to molecular structure and motion. Transition States Theory (TST) does provide a fundamental framework; however, it inevitably leads to the Arrhenian temperature dependence disqualifying it as a viable candidate for describing glassy behavior. One of the implicit assumptions of the TST is that of a system being in contact with a thermal bath. Alternatively, we investigate a system where instead of the thermal bath an element can only acquire the "kinetic energy" necessary for a transition to a higher energy state from its immediate neighbors via thermal exchange.

The dynamical behavior of the system is modeled as a sequence of Monte Carlo updates. When the energy transfer between adjacent elements can take place both from the element with higher "kinetic energy" to the element with the lower one and vice versa, the Arrhenian behavior of the relaxation times is recovered at all temperatures. However, when the energy exchange is directional, proceeding only from the element with higher "kinetic energy" to the element with the lower one, the Arrhenian dependence is only observed at high temperatures. As the temperature decreases the longest relaxation time, determined via autocorrelation function decay, appears to diverge at a finite temperature, which corresponds to vanishing of the configurational entropy of the system. The WLF function provides an excellent fit to the predicted temperature dependence of the relaxation time over the entire simulation range. The conditions under which the directional transfer of the local kinetic energy can occur in real systems and its possible experimental manifestations will be discussed.

## **Symposium DS Dilute Solutions**

Organizers: Graham M. Harrison and Matteo Pasquali

Monday 1:50 Room 107

DS6

### **Study of the effects of drag-reducing polymers on flow of red blood cells in tubes**

Joie Marhefka, Philip Marascalco, and Marina V. Kameneva

*McGowan Institute for Regenerative Medicine/Bioengineering, University of Pittsburgh, Pittsburgh, PA 15219*

It was discovered several decades ago that the addition of minute amounts of certain soluble polymers, so called drag-reducing polymers (DRPs), to fluid significantly decreases flow resistance in turbulent flow conditions. Blood soluble DRPs were also demonstrated to have the ability to increase blood flow and tissue oxygenation with no direct effect on vessel tone when injected at nanomolar concentrations in various animal models of normal and especially pathological circulation. Several polymers with high molecular weights and fairly linear structures but chemically dissimilar monomers, including polyethylene oxide, polyacrylamide, and certain polysaccharides, were shown to facilitate blood flow in vitro in pipes and in vivo. Thus, the mechanisms of the DRP effects, both in turbulent flow and in the vascular system, are likely based on specific mechanical and fluid dynamic properties of the polymers rather than on the chemical composition of the molecules.

Elucidation of the mechanisms of the observed beneficial DRP effects on blood circulation is extremely important for potential clinical application of these polymers. The effects of the DRPs on flow behavior of red blood cells (RBCs) were studied in tubes of various sizes, orientations, and geometries at various flow conditions. In turbulent flow in large tubes, the DRPs significantly reduced resistance to flow of RBC suspensions. In small capillary tubes, we tested our hypothesis that one of the mechanisms behind the DRP effect on microcirculation is that DRPs cause a redistribution of the RBCs across the microvessels. These studies demonstrated that DRPs promoted moving RBCs closer to the walls, leading to a reduction of the near-wall plasma layer, which in vivo might facilitate gas transport from RBCs to the vessel wall and vice versa. Also, due to an increase in the near-wall hematocrit and viscosity, this effect produces an increase in wall shear stress in the microvessels, potentially promoting vasodilation and decreasing vascular resistance.

Monday 2:15 Room 107

DS7

### **Capillary thinning rheometry**

Michael S. Owens, Wieslaw Suszynski, L. E. Scriven, and Christopher W. Macosko

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

Characterizing the viscoelastic properties of dilute polymer solutions, by experiment, is challenging. We have found that weak elasticity, which can significantly effect coating performance, is undetectable by modern shear rheometers. Yet it is easily observed during capillary thinning experiments. Although capillary thinning is remarkably sensitive to elasticity its limitations have not been defined. We present an analysis of the working equations for viscopillary and elastopillary thinning of Newtonian and viscoelastic liquids, respectfully.

Materials spanning a wide range of viscosity, surface tension, and elasticity were used to define the practical limitations of this technique as well as compare capillary thinning to other extensional indexers.

Monday 2:40 Room 107

DS8

### **Modeling and experiments of electrostatically driven Boger fluid jets**

Colman P. Carroll and Yong L. Joo

*School of Chemical & Biomolecular Engineering, Cornell University, Ithaca, NY 14853*

Electrostatic fiber spinning or 'electrospinning' is a novel process forming polymeric fibers with submicron scale diameters through the action of electrostatic force. To investigate the influence of the viscoelasticity on the electrohydrodynamics in electrospinning, well characterized Boger fluids have been used. The effect of the electric conductivity of the fluids on the jet profiles has also been studied. In our model for the electrospinning process, viscoelastic models for polymer solutions such as Oldroyd-B and FENE-P models are fully coupled with momentum equations and Gauss' law. We have derived those equations based on thin filament approximation and the system of differential equations governing electrically charged, stable polymeric jets have been numerically solved using a multiple shooting method. The simulation results such as fiber diameter predicted with Oldroyd-B and FENE-P models are compared with the experimental data.

Monday 3:05 Room 107

DS9

### **An approximate solution to flow through a contraction for high Trouton ratio fluids**

Alex S. Lubansky<sup>1</sup>, David V. Boger<sup>1</sup>, and Justin J. Cooper-White<sup>2</sup>

<sup>1</sup>*Particulate Fluids Processing Centre, The University of Melbourne, Melbourne, Victoria 3010, Australia;* <sup>2</sup>*Division of Chemical Engineering, The University of Queensland, St Lucia, Queensland 4072, Australia*

An approximate analytical solution to predict the flow, vortex and pressure drop behaviour in abrupt axisymmetric contractions is presented. The predicted flow characteristics are compared to available experimental results from the literature. This solution is developed to identify the effect of fluids which exhibit large Trouton ratios at large extensional rates despite having a constant shear viscosity. This behaviour approximates that shown in dilute solutions of polymeric liquids, although it smooths any transient effects by assuming that the steady-state extensional viscosity undergoes a step change from a Trouton ratio of 3 to a large Trouton ratio at a critical rate. The formalism predicts that the vortex behaviour is determined principally by the fluid's characteristic time, whilst the steady-state extensional viscosity determines the pressure drop, suggesting that transient extensional effects do not impact the resultant pressure drop. The predicted pressure drop shows good agreement with available experimental results up to the observed onset of elastic flow instabilities.

## **Symposium SC Suspensions and Colloids**

Organizers: Jan Vermant and Dan Klingenberg

Monday 3:55 Room 107

SC1

### **Interparticle attractions and the zero shear viscosity of near hard sphere colloidal dispersions**

Norman J. Wagner<sup>1</sup>, Lakshmi Krishnamurthy<sup>1</sup>, and Jan Mewis<sup>2</sup>

<sup>1</sup>*Chemical Engineering, University of Delaware, Newark, DE 19716;* <sup>2</sup>*Department of Chemical Engineering, K.U. Leuven, Leuven B-3001, Belgium*

This presentation addresses the question as to whether the zero shear viscosity diverges at the colloidal glass transition or at random close packing. We explore the effects of van der Waals attraction on the zero shear viscosity of colloidal suspensions to address the reported discrepancies in the literature concerning various "hard sphere" dispersions. The non-trivial contribution of short-range, weak attractions to the viscosity arises from indirect effects on the free volume in the dispersion. Mode coupling predictions for the glass transition are used within a semi-

Monday Afternoon

empirical model to predict the effect and are compared with measured divergences of the zero shear viscosity. Reasonable agreement is observed with Hamaker constants calculated from material properties, but questions remain about the analytical form of the viscosity divergence.

Monday 4:20 Room 107

SC2

### **Yielding and flow of colloidal glasses and gels**

Khoa Pham<sup>1</sup>, George Petekidis<sup>2</sup>, Peter N. Pusey<sup>1</sup>, and Dimitris Vlassopoulos<sup>2</sup>

<sup>1</sup>*School of Physics, University of Edinburgh, Edinburgh, United Kingdom;* <sup>2</sup>*Institute of Electronic Structure & Laser, FORTH, Heraklion, Crete 71110, Greece*

We report on some rheological properties of suspensions of hard-sphere colloids with particular reference to behaviour near the concentration of the glass transition. We identify the yield stress of the glass and find that it compares favourably with the predictions of a recent mode coupling treatment of sheared suspensions. Further, using creep and recovery experiments we find that, at all values of the applied step stress, colloidal glasses show a rapid elastic recovery of strain after the stress is removed. With increasing stress, the magnitude of this recovered strain saturates at a surprisingly large value of 10-20%. We attribute this behaviour to "cage elasticity", the recovery of the stress-induced distorted environment of any particle to a more isotropic state when the stress is removed. Finally, we apply the same experimental protocol to high volume fraction colloid-polymer mixtures, which can form repulsive or attractive glasses with increasing polymer concentration. Interestingly, the yield strains of both attractive and repulsive glasses are almost the same. On the other hand, lower volume fraction colloid-polymer gels exhibit a much lower yield strain. This serves as a distinction between gels and glasses. We also discuss the volume fraction dependence of the elastic moduli of these glasses.

Monday 4:45 Room 107

SC3

### **Structural evolution and non-linear rheology of weak colloidal gels during start-up of steady shear flow**

Ali Mohraz and Michael J. Solomon

*Department of Chemical Engineering, The University of Michigan, Ann Arbor, MI 48109*

The transient structural evolution of fractal colloidal gels during start-up of steady shear flow is quantified by flow light scattering and rheometry. The model materials are fractal cluster gels of colloidal spheres, aggregated by the diffusion-limited cluster aggregation (DLCA) mechanism. Time-resolved flow light scattering shows three regimes of structural evolution in the velocity-gradient plane: near-affine deformation, rupture, and cluster densification. Structural anisotropy in the first regime is significant, and displays universal scaling with the applied strain. Flow cessation experiments at  $Pe \ll 1$  in this regime do not show relaxation to isotropic structure. In the second regime the anisotropy attains a maximum, which is identified as the gel rupture point. Rheological measurements demonstrate that this point coincides with a sharp maximum in the shear stress. The volume fraction dependence of the critical rupture strain as extracted from light scattering and rheological measurements displays the scaling  $1+0.6\gamma_c \sim \phi^{(1-x)/(3-Df)}$ , where  $x$  and  $Df$  are the backbone and cluster fractal dimensions, respectively. The observed scaling is different from that found earlier for the linearity limit, and agrees with the simple model of gel rupture occurring after the cluster backbone is extended to its full length. Qualitative differences between the transient anisotropy of colloidal gels comprised of colloidal spheres and rods are observed. The findings suggest that the microstructural origin of the large anisotropy and in colloidal sphere gels upon non-linear deformation is the relative angular displacements of particles in the singly connected regions of the gel backbone.

Monday 5:10 Room 107

SC4

### **Times scales and aggregation mechanisms in a Laponite-poly(ethylene oxide) dispersion under shear flow**

John R. de Bruyn<sup>1</sup>, Frédéric Pignon<sup>2</sup>, Jean-Michel Piau<sup>2</sup>, and Albert Magnin<sup>2</sup>

<sup>1</sup>*Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada;* <sup>2</sup>*Laboratoire de Rhéologie, CNRS UMR 5520, INPG and UJF, Grenoble 38041, France*

Recent studies of polymer-colloid composite materials under shear or extensional flow have been motivated by their spectacular rheological behavior and extensive industrial applications. The aim of this work is to examine the

influence of shear flow on structural changes in Laponite-polyethylene oxide dispersions at the micron length scale, and to link these with their macroscopic properties. Bulk rheometric measurements were combined with static light scattering in the dispersions under shear flow. From rheometric measurements the time scales that characterize the material's response to step changes in shear rate have been identified. These time scales are interpreted in terms of a competition between aggregation and bond formation mechanisms between the clay particles and polymer chains. A critical shear rate separates two regions with different rheological behaviors. A qualitative change in the anisotropy of the dispersion under shear, studied by static light scattering, is observed at the same critical shear rate. Above this shear rate, shear enhances the interactions between clay particles and polymer chains, giving rise to the aggregation and orientation of micron scale aggregates.

## Symposium BS Biological Systems

Organizers: Panos Dimitrakopoulos and Eric Furst

Monday 1:50 Room 108/109

BS6

### **Using multiple particle tracking to study extracellular matrices**

Patrick S. Doyle and Thierry Savin

*Chemical Engineering, MIT, Cambridge, MA 02139*

We have used a multiple particle tracking technique (MPT) to study the local properties of artificial and natural extra cellular matrices (ECM) far from equilibrium. We have focussed our study on two experimental systems. First we performed MPT on particles embedded in the artificial ECM scaffold formed by custom designed oligopeptides. We followed the matrix during its self-assembly and interrogated the spatial heterogeneity of the microenvironment. Second, MPT was applied on beads dispersed in a natural ECM extract, that was degraded by the addition of matrix metalloproteases, thus mimicking a natural route used by migrating cells.

Monday 2:15 Room 108/109

BS7

### **Microstructural and microrheological properties of novel self-assembled hydrogels**

Cecile Veerman<sup>1</sup>, Karthikan Rajagopal<sup>2</sup>, Joel P. Schneider<sup>2</sup>, and Eric M. Furst<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Delaware, Newark, DE 19716;* <sup>2</sup>*Department of Chemistry and Biochemistry, University of Delaware, Newark, DE*

Hydrogels are an important class of materials that have extensive uses in tissue engineering and drug delivery applications. Recently, a short 20 amino acid b-hairpin peptide (MAX 1) have been designed for the preparation of novel hydrogels, that reversibly folds and gel by a process of hierarchical self-assembly. Little is known of the gelation kinetics and microstructure of these complex materials. A better understanding on a microscopic level is necessary for insight into dynamics and mechanical properties that control many chemical and physical processes. In this study, the microrheology of self-assembled hydrogels were investigated while varying the pH and ionic strength. With the use of multiple particle tracking, insight was obtained into the gelation kinetics and microstructure. Also, the effects of surface chemistry of the tracer particles on the microstructure and gelation kinetics were investigated. Tracer particle mobilities were analysed within the framework of one- and two- point microrheology. An increasing gelation time with decreasing peptide concentration was found. The van Hove correlation function was used to get more insight in the microenvironment of the hydrogel. A deviation from Gaussian behavior was observed, indicating heterogeneity in the mechanical response. Microrheological techniques enable us to understand the mechanical properties of hydrogels at a microscopic level. Greater insight in these properties allows the design of novel peptides, until the ultimate microstructural and microrheological properties are obtained for tissue engineering and drug delivery applications.

Monday 2:40 Room 108/109

BS8

**Active and passive microrheology of semiflexible fd virus solutions**

Karim M. Addas<sup>1</sup>, M. Keller<sup>2</sup>, Erich Sackmann<sup>2</sup>, Christoph F. Schmidt<sup>3</sup>, and Jay X. Tang<sup>4</sup>

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We compare an active and a passive microrheology method for solutions of monodisperse semiflexible, filamentous fd virus. The passive technique relates the thermal fluctuations of single, laser trapped, micron sized beads to the complex shear modulus of the solution. In the active method, an oscillatory magnetic force is applied to a single micron sized magnetic bead and the complex shear modulus is derived from the response of the bead. Measurements are also shown for a rotating disk macrorheology technique. Agreement between the three methods is observed.

Monday 3:05 Room 108/109

BS9

**Relaxation mechanism of extended biopolymers**

Panagiotis Dimitrakopoulos and Inuka D. Dissanayake

*Department of Chemical Engineering, University of Maryland, College Park, MD 20742-2111*

The present study considers the conformational relaxation of a single flexible or stiff polymer chain from an initial straight configuration in a viscous solvent. This problem commonly arises when strong flows are turned off in both industrial and biological applications. The problem is also motivated by recent experiments with single DNA molecules relaxing after being fully extended by applied forces as well as by the recent development of micro-devices involving stretched tethered biopolymers. Our interest lies on understanding the relaxation mechanism for flexible and stiff polymers, and thus our results are applicable to a wide array of both synthetic polymers as well as biopolymers such as DNA, actin filaments, microtubules and rodlike viruses.

In recent years considerable progress has been made in understanding the properties of semiflexible polymers near equilibrium. With this study, we want to understand the relaxation mechanism of a specific problem far from equilibrium where a complete theory of the relaxation process is lacking. We show that the early longitudinal relaxation, being associated with a quasi-steady relaxation of link tensions of Brownian nature, is valid for any chain stiffness. Stiff chains are shown to exhibit a late longitudinal relaxation associated with the cumulative effect of the deforming Brownian forces and the restoring bending forces on the link tensions. We also show how from the knowledge of the relaxation mechanism, we can predict and explain the polymer properties including the polymer stress and the solution birefringence. A generalized stress-optic law is derived valid for any time and chain stiffness. The inherent nonlinearity of the current problem is shown to result in a nonlinear force-extension relation for both flexible and stiff chains. The techniques we develop to understand the relaxation mechanism may be useful for a wide array of problems in polymer rheology.

Monday 3:55 Room 108/109

BS10

**Rheological studies of nano-hydroxyapatite suspensions for biomedical applications**

Kothapalli Chandrasekhar<sup>1</sup>, Joseph Paguio<sup>2</sup>, Antonio E. Senador<sup>3</sup>, Mei Wei<sup>1</sup>, and Montgomery T. Shaw<sup>3</sup>

<sup>1</sup>*Department of Metallurgy and Materials Engineering, University of Connecticut, Storrs, CT 06269-3136;* <sup>2</sup>*Lamar University, Beaumont, TX;* <sup>3</sup>*Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269*

Synthetic hydroxyapatite (HA)-polymer composites can exhibit the mechanical properties and bioactivity analogous to natural bone. Despite the promising potential applications of hydroxyapatite composites in biomedical devices, dispersion issues still limit the use of HA. We report here the results of a study of the rheological response (a useful indicator of dispersion) for suspensions of 40 wt% nano HA in 75 wt% glycerol-water solution with a stabilizers based on poly(acrylic acid). Nano-crystalline HA was synthesized by the wet-precipitation method and suspended in glycerol with varying amounts of the stabilizer, Dispex N40, which is 8-kDa poly(acrylic acid) completely neutralized with Na. The concentration of the stabilizer was varied between 0-0.24 wt%, while the degree of neutralization was varied from 0 to 100%. In contrast to the results of Jansma and Qutubuddin (1995) with micron-sized particles, formation of a gel-like structure was observed at around 0.16 wt % addition of neutralized PAA

(NaPAA) in the 40 wt% (22 vol%) HA-glycerol system. The transformation from fluid-to gel-like behavior occurred over a very narrow concentration range of the NaPAA; no gelation was found for the acid form, i.e., PAA. As the zeta potential of HA particles is positive, we hypothesize that the polymer anions interact strongly with the HA surface, forming a percolated network. The concentration dependence of the linear viscoelastic properties will be presented along with comparison with scaling theory for percolation in suspensions.

Jansma, J. B. and S. Qutubuddin, "Rheological behavior of concentrated calcium halophosphate suspensions," *J. Rheol.* 39 (1995)

Monday 4:20 Room 108/109

BS11

### **Characterization of polymer hydrogels formed via saccharide-peptide interactions**

Byeong Seok Chae<sup>1</sup>, Nori Yamaguchi<sup>2</sup>, Kristi L. Kiick<sup>2</sup>, and Eric M. Furst<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Delaware, Newark, DE 19716;* <sup>2</sup>*Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716*

The understanding and ability to control the microstructure and microscale response plays a critical role in synthesis and processing of polymeric materials. A long-standing aim has been to identify the fundamental roles that nano- and microscopic interactions and structure play in determining bulk properties, such as viscoelasticity, yield stress and non-linear behavior. The emerging applications of polymers in drug delivery and tissue engineering will require not only control of bulk material properties, but the rational design of microstructure and microscopic mechanical responses, molecular delivery kinetics and functionality on the length and timescales of cellular processes. Here, we report studies of both the macro- and micro-rheology of a novel class of heparin-decorated polymers whose assembly, rheological properties, and delivery profiles are controlled by specific peptide-saccharide interactions. The elastic modulus is found to increase significantly with the addition of polymers decorated with complementary peptide sequences that bind heparin, and correlates with the measured binding affinity. Using laser-tweezer microrheology, we show that the microstructure of the network is heterogeneous on the scale of micrometers to tens of micrometers, with interstitial regions of water spanned by rigid fibrils. Such properties may be amenable for nutrient and waste transport, while providing distinct scaffolds for cell adhesion and motility.

Monday 4:45 Room 108/109

BS12

### **Molecular and rheological characterization of hyaluronic acid and equine synovial fluid**

Danielle Leiske<sup>1</sup>, Sara Tracy<sup>1</sup>, Heidi Schmidt<sup>1</sup>, Jill Parker<sup>2</sup>, and Skip Rochefort<sup>1</sup>

<sup>1</sup>*Chemical Engineering Department, Oregon State University, Corvallis, OR 97331;* <sup>2</sup>*College of Veterinary Medicine, Oregon State University, Corvallis, OR 97331*

Hyaluronic acid (HA) is a polysaccharide found in all parts of the body. As the major high Mw component of synovial fluid, HA is responsible for the viscoelastic properties important in joint lubrication and cartilage protection. The molecular (GPC-MALLS) and rheological (steady and dynamic oscillatory shear) characterization of several commercial HA supplements and a number of equine synovial fluid samples will be reported.

The steady and dynamic oscillatory shear properties of nine pure HA solutions were measured at 2.5 mg/ml (above c\*). Most samples reached a zero shear viscosity of approximately 0.008-0.11 Pa-s and entered a shear-thinning region at shear rates between approximately 10-100 s<sup>-1</sup>. In the frequency range of 0.1-15 Hz no samples exhibited a crossover point in the dynamic oscillatory tests. Molecular characterization was completed using GPC-MALLS and intrinsic viscosity measurements. Zero shear viscosity was found to be proportional to (cMw)<sup>1.08</sup>. A Mark-Houwink equation was developed for HA in a phosphate buffer solution.

The results of pure HA characterization were then compared to the rheological properties and molecular characterization of equine synovial fluid (both from live and euthanized horses) in attempt to elucidate the role of HA in joint lubrication. The concentration and molecular weight of the HA-protein complex in the synovial fluid was measured using GPC-MALLS. HA concentrations ranged from 0.13-0.84 mg/ml and molecular weight ranged from 1.5-5×10<sup>6</sup>. Synovial fluid had similar rheological characteristics to HA with a zero shear viscosity region ranging from 0.01-1 Pa-s. We are currently investigating the properties of synovial fluid in normal equine joints to establish baseline values with the intention of determining synovial fluid properties in animals with joint disease before and after treatment.

Monday Afternoon

Monday 5:10 Room 108/109

BS13

**Study of the effects of blood soluble drag-reducing polymers (DRPs) on blood viscoelastic and coagulation parameters**

Philip Marascalco, Trevor Snyder, Joie Marhefka, and Marina V. Kameneva

*McGowan Institute for Regenerative Medicine/Bioengineering, University of Pittsburgh, Pittsburgh, PA 15219*

The addition of minute concentrations (~1 ug/ml) of special, blood soluble, drag reducing polymers (DRPs) to blood has been shown to increase microcirculatory flow and reduce vascular resistance without affecting vascular tone. Preliminary studies have demonstrated that the intravenous infusion of a DRP solution can restore microcirculatory blood flow and prevent lethality in animals (rats) with experimentally induced severe hemorrhagic shock and increase capillary flow in diabetic animals. The exact mechanisms of the DRP beneficial effects are yet to be elucidated. Here, we are testing a hypothesis that the DRPs affect viscoelastic properties of blood using blood from normal and diabetic rats. We are also investigating the DRP potential effects on the blood coagulation system in normal rats to exclude any deleterious effects on clotting and hemostasis.

Diabetes was induced in rats using streptozotocin (65 mg/kg) and characterized by blood glucose levels above 300 mg/dl (below 200 mg/dl in normal rats). Blood rheological properties (viscosity, elasticity, and relaxation time) of normal and diabetic rats were tested using a Vilastic-3 viscoelastometer and a Wells-Brookfield Cone/Plate viscometer at shear rates from  $\sim 1 \text{ s}^{-1}$  to  $\sim 300 \text{ s}^{-1}$ . Plasma viscosity was measured by a capillary viscometer. We also evaluated the effects of DRPs on a variety of hematological parameters in vitro and in vivo, after DRP administration to rats. Prothrombin time (PT), partial thromboplastin time (PTT), fibrinogen, D-Dimer, CBC differential, and platelet count were measured (Antech Diagnostics) and platelet activation was evaluated by measurement of platelet CD62P using flow cytometry. Clot formation time (in vitro) was evaluated by the time required for clotting of blood samples withdrawn with no anticoagulant and treated with DRPs or equal volume of a vehicle (saline).

The preliminary results demonstrated statistically significant effects of DRPs on viscoelastic properties of blood and no measurable effects on the coagulation system.

**Symposium MF  
Multiphase Fluids**

Organizers: Venkat Ganesan and Sachin Velenkar

Monday 1:50 Theater

MF6

**Rheological study of the influence of shear flow on crystallization of polyhedral oligosilsesquioxanes (POSS) in PEG-based multiblock polyurethanes**

Jian Wu<sup>1</sup>, Qing Ge<sup>2</sup>, Kelly A. Burke<sup>1</sup>, and Patrick T. Mather<sup>3</sup>

<sup>1</sup>*Chemical Engineering, University of Connecticut, Storrs, CT 06269;* <sup>2</sup>*Institute of Materials Science, University of Connecticut, Storrs, CT 06269;* <sup>3</sup>*Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106*

A unique series of thermoplastic polyurethanes (TPUs) was synthesized using poly(ethylene glycol) (PEG) as the polyol and incorporating an isobutyl-functionalized POSS diol as chain extender. The materials were designed based on earlier success in forming materials with crystalline ordering of POSS for a telechelic architecture of similar composition. Preliminary investigations revealed that micro-phase separation occurs between hydrophilic soft segments (PEG) and hydrophobic hard ones (POSS) due to both thermodynamic incompatibility and concurrent crystallization of POSS-rich phase, resulting rheologically in gelation. We investigated this gelation behavior by rheological techniques under different isothermal conditions and shear flow histories always above the PEG melting point but near and below the melting point of the POSS. Isothermal oscillatory experiments revealed critical gelation times, due to POSS crystallization, that featured an Arrhenius temperature dependence. These observations served as an internal reference to reveal the influence of steady shear flow. Imposing isothermal steady-shear flow a shear-rate dependent induction time exists, beyond which the viscosity increases dramatically due to POSS crystallization.

Surprisingly, this induction time increases with shear rate, leveling off at high shear rates. Interrupted shear experiments revealed a similar finding that will be reported in detail. Our results stand in contrast to those for polyolefins crystallizing under the influence of shear where flow generally enhances the rate of crystallization. We attribute this qualitative difference to a difference in crystallization mechanism. While shear flow induces polyolefin chain orientation and enhances nucleation, shear flow of the POSS-based TPUs apparently disrupts melt-state POSS aggregation, leading to a shear-weakened crystallization.

Monday 2:15 Theater

MF7

**Rheological effects of drag-reducing polymers on blood flow in microcirculation**

Marina V. Kameneva

*McGowan Institute for Regenerative Medicine/Bioengineering, University of Pittsburgh, Pittsburgh, PA 15219*

Blood-soluble drag-reducing polymers (DRPs) have been shown to significantly improve microcirculation in animal models when added to blood at nanomolar concentrations. The exact mechanisms behind the beneficial DRP effects on blood circulation remain to be identified. However, some hypotheses regarding the DRP intravascular action were tested. It has been demonstrated that DRPs reduce flow separations at vessel bifurcations (Kameneva et al., 1988, 1990). This effect may reduce pressure loss in arterial vessels and thus increase precapillary pressure promoting an increase in functioning capillary density and tissue perfusion (both observed in animal experiments). Recently, the experiments with flow of red blood cell (RBC) suspensions through microchannels demonstrated a significant decrease in the near-wall cell-free plasma layer due to addition of DRPs. The two-phase nature of blood flow in vessels/tubes with diameters below 0.5 mm is extremely important since it causes a decrease in both microvessel apparent viscosity and hematocrit due to a plasma layer formed near the wall (Fahraeus-Lindquist or F-L effect). The F-L effect, while reducing flow resistance in the pipe, may have negative effects in microvessels diminishing oxygen transport from RBCs to the vessel wall and causing vasoconstriction via reduction in a wall shear stress which is responsible for release of shear-stress dependant vasodilators. The reduction in the cell-free plasma layer due to addition of DRPs to blood may facilitate gas exchange in microvessels via relocation of some RBCs to the near-wall space. In addition, due to an increase in microvessel hematocrit caused by attenuation of a "plasma-skimming" effect, DRPs will increase vessel wall shear stresses potentially promoting vasodilation and an increase in density of functioning capillaries. This phenomenon may have a significant impact in regenerative medicine and tissue engineering representing a novel method of selectively introducing mechanical stimuli on endothelium in microvessels.

Monday 2:40 Theater

MF8

**Rheology and flow-induced structure in a polystyrene-polyisoprene biocontinuous microemulsion**

Kristin Brinker and Wesley Burghardt

*Northwestern University, Evanston, IL*

Polymer bicontinuous microemulsions are blends of immiscible polymers compatibilized with diblock copolymer in such a way as to produce an equilibrium interconnected morphology in which interpenetrating domains of the different species exist at equilibrium length scales on the order of 10s of nanometers. Previous experiments on a microemulsion of poly(ethyl ethylene) (PEE) and poly(dimethyl siloxane) (PDMS) have revealed a fascinating array of rheological and flow-induced structural phenomena. In order to extend the range of polymer microemulsions studied under flow, we have prepared a recipe from low molecular weight polystyrene (PS) and polyisoprene (PI) and their corresponding block copolymer. In symmetric ternary blends, the bicontinuous microemulsion phase is located in a region of high total homopolymer concentration. Despite the fact that the constituent homopolymers are strictly Newtonian, the microemulsion exhibits substantial viscoelasticity associated with flow-induced deformation of the supramolecular organization. The linear viscoelastic properties of the PS-PI microemulsion closely resemble those previously found in the PEE-PDMS system. Under even fairly weakly nonlinear flow conditions, the PS-PI microemulsion exhibits a flow-induced phase transition. In situ small-angle x-ray scattering is used to probe both the flow-induced deformation of the equilibrium microemulsion structure as well as the onset and development of a flow-induced bulk phase separation. The higher susceptibility of the PS-PI system to phase separation may be related to an even higher viscosity contrast between its constituents and those in the previously studied PEE-PDMS system.

Monday 3:05 Theater

MF9

**Phase diagram of non-Brownian carbon nanotube suspensions**Erik K. Hobbie<sup>1</sup>, Dan Fry<sup>1</sup>, and Hao Wang<sup>2</sup><sup>1</sup>*NIST, Gaithersburg, MD;* <sup>2</sup>*Michigan Technological University, Houghton, MI*

The 'phase diagram' of a non-Brownian carbon nanotube suspension is measured as a function of concentration, shear stress, and confinement. We observe a hierarchy of flow-induced structure, including dispersed nematics, a variety of aggregates, and 'jammed' fractal networks. By applying simple scaling arguments to rigid-rod gels, our data suggest that the jamming portion of the network is more diffuse than the full elastic network, akin to 'force chains' in a granular fluid.

Monday 3:55 Theater

MF10

**Measurements of particle orientation in simple shear and channel flows of polypropylene/clay nanocomposites**Laura Dykes and Wesley Burghardt*Northwestern University, Evanston, IL*

Flow-induced changes in the orientation of dispersed clay particles is expected to have a significant effect on the properties of polymer/clay nanocomposite materials. Here we report studies of flow-induced orientation in dispersions of organically modified montmorillonite clay in polypropylene. The nanocomposite samples were prepared using two methods. Melt blending in a twin-screw extruder led to intercalated samples in which the layered structure of the clay remains intact. An additional step of solid-state shear pulverization leads to samples with a much higher degree of exfoliation of individual clay sheets. In situ x-ray scattering was used to probe particle orientation in steady shear using an annular cone and plate shear cell which provides information about particle orientation in the flow-gradient plane. The more highly exfoliated pulverized sample shows significantly lower orientation than the intercalated melt-blended sample. Both samples were also studied in extrusion-fed channel flows. In slit-channel geometries, the dominant shear rate direction is parallel to the x-ray beam, allowing information about orientation in the flow-vorticity plane to be acquired. In fact, little scattering was observed in these configurations, indicating the tendency of clay particles to 'lie down' in the shear flow. Superposition of extension via contractions or expansions in slit-channel flows did not reorient particles sufficiently to bring them 'into view' in these geometries. Extrusion experiments using a nominally two-dimensional slit flow, in which the beam passes along the vorticity direction, provided the means to obtain orientation data in these samples at higher shear rates than the annular cone and plate shear cell.

Monday 4:20 Theater

MF11

**Investigating filler reinforcement and nonlinear viscoelastic behavior of silica particle filled polybutadiene**Zhiyong Zhu<sup>1</sup>, Thaddeus Thompson<sup>1</sup>, Shi-Qing Wang<sup>1</sup>, Ernst von Meerwall<sup>2</sup>, and Adel Halasa<sup>3</sup><sup>1</sup>*Polymer Science, University of Akron, Akron, OH 44325-3909;* <sup>2</sup>*Physics, University of Akron, Akron, OH 44325-3909;* <sup>3</sup>*Goodyear Tires & Rubbers, Akron, OH*

We explore the well-know phenomena of filler reinforcement (i.e., increase of elastic modulus  $G'$  due to incorporation of fillers) and Payne effect (i.e., decrease of  $G'$  at large strain amplitudes) in terms of the matrix molecular weight, filler loading, and time scales used to probe the viscoelasticity of filled melts. Use of monodisperse non-crosslinked 1,4-polybutadiene (PBD) along with a silica filler allows illustration of different mechanisms of filler reinforcement in the elastic and liquid regimes. Specifically, the enhancement of  $G'$  relative to that of the pure matrix grows linearly with the filler volume fraction  $\phi$  in the elastic plateau region (equivalent to a crosslinked sample).  $G'$  goes as  $\phi^{3.4}$  in the terminal region where the pure matrix is liquid like. Comparing the suspension involving a small molecule medium of dioctyl phthalate with the filled PBD shows that the filler reinforcement is mainly due to filler aggregation. Also illustrated is the role of chain bridging between fillers that can greatly enhance the elastic response in the terminal region at high filler loadings. The Payne effect, i.e., decrease of  $G'$  with increasing strain amplitude  $\gamma$  of shear oscillation, is seen to be time-dependent and comprised of an instantly recoverable component (inherent) and a slowly recovering component associated with the disruption of the filler-filler association. Examining  $G'$  at both high and low strain amplitudes through stepwise ramping allows us to

reveal (a) filled melts are inherently less elastic at large  $\gamma$  and (b) recovery of  $G'$  after high amplitude oscillatory shear is likely to involve chain adsorption and re-bridging.

Monday 4:45 Theater

MF12

**Mobility and in situ aggregation of charged microparticles at oil-water interface**

Sowmitri Tarimala, Srinivas Ranabothu, Jeremy Verneti, and Lenore L. Dai

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409*

Particle mobility, aggregate structure, and the mechanism of aggregate growth at the two-dimensional level have been of long-standing interest. Here we use solid-stabilized emulsions as a model system to investigate the mobility of charged microparticles at polydimethylsiloxane (oil)-water interfaces using confocal laser scanning microscopy. Remarkably, the rate of diffusion of the charged colloidal-sized polystyrene particles at the oil-water interface is only moderately slower than in the bulk water phase. The ambient diffusion constant of solid particles is significantly reduced from  $1.1 \times 10^{-9} \text{ cm}^2/\text{s}$  to  $2.1 \times 10^{-11} \text{ cm}^2/\text{s}$  when the viscosity of the oil phase increases from 5 cSt to 350 cSt. In addition, we successfully observe the in-situ structural formation of solid particles at the oil-water interface.

Monday 5:10 Theater

MF13

**Higher harmonics in large amplitude oscillatory shear response**

Kyung H. Ahn, Kyu Hyun, Eunsu Baek, Kwangsoo Cho, and Seung J. Lee

*School of Chemical Engineering, Seoul National University, Seoul, Republic of Korea*

Complex fluids form complex microstructures depending on their thermal and deformation history conditions, which leads to diverse rheological properties. The measurement of  $G'_i$  and  $G''_i$  is often the most useful way of characterizing the complex fluids. The moduli are usually predicted by molecular theories, and exorbitant number of experiments has been carried out to elucidate the microstructure of complex fluids. One of the nonlinear experiments is the large amplitude oscillatory shear (LAOS). As storage modulus  $G'_i$  and loss modulus  $G''_i$  are defined only in the linear viscoelastic regime, the moduli at large strain lose mathematical background, and have normally been neglected. However, provided that enough care is taken, LAOS test can provide plentiful amount of additional information. In addition, it allows both strain amplitude and time scale to be controlled independently, and it is easy to generate because it does not involve any sudden jump in speed or position. In this talk, we will compare the rheological properties in both linear and nonlinear regime. We will show the abundance of information on the microstructure in the nonlinear regime, and the importance of LAOS experiment in revealing the interaction within the complex fluids as well as in characterizing the complex fluids.



# Tuesday Morning

## Symposium PL Plenary Lectures

### *Bingham Lecture*

Tuesday 8:30 Theater

PL2

#### **Rheometry: From concentric cylinders to optical tweezers**

Christopher W. Macosko

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

This presentation will review the development of rheometry from its historical roots to our current instruments and speculate a bit on its future. I will start with the origins of early rotational rheometers; Couette's was not the first! I will trace their evolution from using manometers and mirrors reflected onto meter sticks to computer aided analysis and control. My efforts with Joe Starita in this adventure will receive disproportionate emphasis. I will identify some current challenges and suggest possible future directions.

## Symposium GP 50 Years of WLF: Glassy Polymers & Related Systems

Organizers: Sinee Simon and Ed Quitevis

Tuesday 9:45 Room 104/105

GP14

#### **Energy landscape picture of overaging and rejuvenation in a glass**

Daniel J. Lacks and Mark Osborne

*Dept. of Chemical Engineering, Case Western Reserve University, Cleveland, OH*

Molecular simulations and an energy landscape analysis are used to investigate the effects of shear on aging in a glass. Shear beyond the yield point is shown to change the state of a glass such that it resembles (but is not identical to) a different stage in the aging process. A cycle of large strain rejuvenates the glass by relocating the system to shallower energy minima, while a cycle of small strain overages the glass by relocating the system to deeper energy minima. The balance between overaging and rejuvenation is controlled by how well the glass was initially annealed.

Tuesday 10:10 Room 104/105

GP15

#### **Enhanced cooperativity below the caging temperature of glass-forming liquids**

Brian M. Erwin<sup>1</sup>, Ralph H. Colby<sup>1</sup>, Sudesh Y. Kamath<sup>2</sup>, and Sanat K. Kumar<sup>3</sup>

*<sup>1</sup>Materials Sci. & Eng. and the Materials Research Institute, The Pennsylvania State University, University Park, PA 16802; <sup>2</sup>Department of Chemistry, The University of Tennessee, Knoxville, TN 37996; <sup>3</sup>Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180*

A cooperative mechanism is invoked to explain the acute property changes observed in glass-forming liquids near the glass transition temperature  $T_g$ . This theory implies the existence of cooperatively rearranging regions (CRR) as characterized by a dynamic length scale  $\xi$ , which is present in both experiments and simulation. Armed with the

Tuesday Morning

temperature dependence of this length scale and the fractal dimension of the CRR (from simulations) a simple scaling model for glassy behavior can be constructed. Using characteristics and previous measurements  $\xi$ , this scaling model has been applied to estimate the  $\xi(T)$  for numerous glass forming liquids.

Tuesday 10:35 Room 104/105

GP16

**Non-linear changes in specific volume: A route to resolve an entropy crisis**

Sanjay Rastogi

*Chemical Engineering, Eindhoven University of Technology, Eindhoven, North Brabant 5600MB, The Netherlands*

The existence of a re-entrant phase diagram, possessing a high temperature and high pressure maximum, will be reported for a polymer, poly(4-methyl-1-pentene). This re-entrant phase behaviour recalls the general phase diagram proposed by Tammann in 1903. Within this phase diagram a region, referred to as the re-entrant region, exists where the entropy of a crystal is greater than that of its liquid. The existence of a crystal having entropy greater than its liquid is in contradiction to the Kauzmann paradox. Here we show how a re-entrant phase diagram can exist without invoking a paradox, this requires a detailed study on the origin of the re-entrant phase behaviour. Tammann ascribes the origin of the re-entrant behaviour, depicted in a pressure-temperature diagram, to the existence of a line where the difference in specific volume between the liquid and the crystal is zero ( $DV = 0$  line) and another line where the difference in enthalpy between liquid and crystal is zero ( $DH = 0$  line). Here we provide direct experimental evidence for the existence of this  $DV = 0$  line for the first time. The experimental observations also show the presence of a second  $DV = 0$  line at lower temperatures. This second  $DV = 0$  line has an essential role in resolving the apparent entropy crisis in the re-entrant region of the pressure-temperature phase diagram, through a relationship between the specific volume and the entropy. These two  $DV = 0$  lines, when combined with the melting and glass transition temperature, describe the shape of the pressure-temperature phase diagram of this polymer.

Tuesday 11:00 Room 104/105

GP17

**Predicting engineering properties in glassy networks from molecular-based parameters**

Alan J. Lesser and Kevin Calzia

*Polymer Science & Engineering Dept., University of Massachusetts, Amherst, MA 01003*

Recent findings suggest that the yield behavior of glassy networks is governed primarily by two molecular based parameters. The first of these parameters is the glass transition temperature,  $T_g$ , and reflects the network stiffness including backbone stiffness, crosslink density, crosslink functionality, and other inter and intra-molecular interactions. The second of these parameters is the cohesive energy density,  $E_c$ , reflects the cohesive strength of the network. In this paper, we present a framework to incorporate these parameters in a molecular-based yield model. We extend the framework to include alterations in temperature, strain rate, stress state, and molecular composition (through these parameters). We also outline current experiments to evaluate the limits and capabilities of the hypothetical model presented and summarize recent findings. Finally, we discuss limitations and opportunities for other engineering properties both linear and nonlinear in form.

Tuesday 11:25 Room 104/105

GP18

**Nonlinear response of glassy polymers: Microscopic origins of torque, normal force and volume changes in torsion**

Anny L. Flory and Gregory B. McKenna

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

Simultaneous torque, normal force and volume change measurements were made as a function of deformation and temperature in a series of polymeric glasses with different chemical structures. A large normal force with a fast relaxation rate was found in two n-alkyl methacrylates, PMMA and PEMA that could not be explained with the very small change in volume observed during torsion. When the measurements are expanded to polycarbonate and polysulfone, no difference is observed between torque and normal force behaviors. The results show that the normal force response in PMMA and PEMA is influenced by their large sub-vitreous  $\beta$  relaxation which has been attributed to side chain motions. In this work, we analyze the data in the context of a time dependent modification of Rivlin's finite elasticity model which allow us to extract the first and second derivatives of the strain energy density function,  $W_1$  and  $W_2$ . Very interestingly, polycarbonate and polysulfone exhibit a behavior closed to neoHookean  $W_2 = 0$

while for PMMA and PEMA  $N_2$  decreases with time. The microstructural origins of these behaviors will be discussed.

## Symposium SC Suspensions and Colloids

Organizers: Jan Vermant and Dan Klingenberg

Tuesday 9:45 Room 107

SC5

### **Polymer molecular weight effects on the rheology of Laponite-PEO dispersions**

Hossein A. Baghdadi and Surita R. Bhatia

*Chemical Engineering, University of Massachusetts, Amherst, MA 01003-9303*

We present rheological data on a model clay-polymer system, an aqueous dispersion of laponite RD with added polyethylene oxide (PEO), which is known to adsorb on the clay surfaces. In our systems, the PEO molecular weight is varied from 13,000 g/mol to 1,070,000 g/mol at a constant clay concentration of 2.0 wt%. We find that low to moderate molecular weight PEO significantly slows down gelation and decreases the elastic modulus,  $G'$ , of the dispersion. Higher molecular weight PEO substantially increases  $G'$  due to formation of a transient network with PEO bridging the clay particles. We believe that short PEO chains form an adsorbed layer that provides a steric barrier to electrostatic aggregation of clay particles, thus preventing or slowing gel formation. At higher molecular weights, PEO chains are long enough to bridge between particles and form an associative network, enhancing the viscosity and elasticity. Finally, we show that the critical molecular weight for this to occur scales as the end-to-end distance of the polymer over the average distance between laponite particles, as might be expected.

Tuesday 10:10 Room 107

SC6

### **Effects of brush grafting density and matrix chain length on wetting/rheology of coated nanospheres in PDMS melts**

David L. Green<sup>1</sup> and Jan Mewis<sup>2</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904;* <sup>2</sup>*Department of Chemical Engineering, K.U. Leuven, Leuven B-3001, Belgium*

Engineered nanocomposites are often formulated by grafting polymer brushes to the surfaces of colloids to optimally disperse them into viscous polymer matrices. In spite of the ubiquity of these filled materials, the essential mechanisms in producing an optimal dispersion have not been well quantified. To this end, rheological and light scattering measurements are made to connect the static wetting and dynamic flow properties of polydimethylsiloxane (PDMS)-grafted silica nanospheres in PDMS melts. By controlling the brush grafting density and the matrix chain length of these model systems, the results indicate that the wetting and the flow behaviors can be quantifiably linked. Overall, these studies represent new ways of quantifying the factors that control the dispersion of polymer-grafted nanoparticles in viscous melts.

Tuesday 10:35 Room 107

SC7

### **Non-Einstein like behavior of nanoscopic sized fillers in polymer melts**

Anish Tuteja<sup>1</sup>, Michael E. Mackay<sup>1</sup>, Craig J. Hawker<sup>2</sup>, and Brooke van Horn<sup>2</sup>

<sup>1</sup>*Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824;* <sup>2</sup>*IBM Almaden Research Center, San Jose, CA 95120*

The effect of adding micron scale or larger fillers on the rheological properties of polymer melts has been extensively studied. Einstein first predicted an increase in the viscosity of suspensions which has been confirmed, not only for suspensions but also for polymeric melts, many times. However, it was recently found that addition of nanoparticles to materials can cause changes in various properties which could not be accounted for using traditional models. For example, Roberts and coworkers showed that addition of small silicate clusters (0.35 nm radius) caused a viscosity decrease in linear poly-dimethylsiloxane while bigger clusters (2.0 nm radius) increased the viscosity. Here, we investigate the effect of the addition of shape persistent polystyrene (PS) nanoparticles, synthesized by

intramolecular crosslinking of linear PS, to linear PS, creating a blend which eliminates enthalpic interactions between the components. This system is thus ideal to delineate the effect of particle size on the properties of the blend. Various methods like small angle neutron scattering (SANS) and differential scanning calorimetry (DSC) are used to establish the absence of phase segregation (depletion flocculation) in the nanoparticle-polymer blend. We previously found that nanoparticles reduce the viscosity of high molecular mass linear PS when the interparticle gap is smaller than the linear polymer size. In the present study we find that addition of the nanoparticles can cause the viscosity of the polymer melt to increase, decrease or remain constant depending on the molecular weight of the linear polymer (entanglements) and the volume fraction of nanoparticles added; in contrast to Einstein's century old prediction. A mechanism accounting for these observed changes in viscosity is also proposed.

Tuesday 11:00 Room 107

SC8

### **Rheology of polyolefin coated aluminum nanoparticles suspensions**

Baptiste Mary<sup>1</sup>, Charles Dubois<sup>1</sup>, Pierre J. Carreau<sup>1</sup>, and Patrick Brousseau<sup>2</sup>

<sup>1</sup>*Chemical Engineering Department, École Polytechnique de Montréal, Montréal, Quebec H3T 1J4, Canada;* <sup>2</sup>*École Polytechnique de Montréal, Montréal, Quebec H3T 1J4, Canada*

Ultrafine aluminum powders have been identified as very promising fuels for novel energetic materials formulations. However, the large specific surface area that gives these powders a high reactivity also makes them particularly difficult to maintain in an unoxidized state and different coating processes have been proposed to solve this problem. The rheology of viscous suspensions of nanoparticles still remains poorly understood and the effect of the coating of these powders on the flow behavior is even more difficult to assess. We have studied the rheology of ultrafine aluminum suspensions prepared from two low molecular weight polymers of different viscosities: a hydroxy-terminated polybutadiene and a polypropylene glycol. The nanosize aluminum powders had previously been coated by a thin layer of high density polyethylene using an in-situ polymerization process. Polypropylene coatings were also obtained. The rheological characterization of the suspensions was conducted by the means of steady and oscillatory shear flow measurements for similar concentrations of non-coated and coated particles. The effect of the coating process on the steady shear viscosity of the suspensions is discussed in terms of the interactions between the particles and the suspending fluids.

Tuesday 11:25 Room 107

SC9

### **Steady state and transient rheological behavior of organoclay-polypropylene nanocomposites**

Simona Ceccia<sup>1</sup>, Jan L. Vermant<sup>1</sup>, and Pier Luca Maffettone<sup>2</sup>

<sup>1</sup>*Department of Chemical Engineering, K.U. Leuven, Leuven B-3001, Belgium;* <sup>2</sup>*Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino I-10129, Italy*

Nanocomposite materials show improved mechanical properties compared to normal composites. Adding sized solid particles to a polymer matrix is known to dramatically alter the rheological properties. In the present work, linear viscoelastic, steady state and transient rheological properties of an organoclay-polypropylene are investigated. The system under investigation consists of montmorillonite dispersed in polypropylene using maleic anhydride grafted polypropylene as a compatibilizer. Above a critical concentration the silica-particles form a network through the polymer matrix and a characteristic solid like behaviour is obtained, as exemplified by the occurrence of a yield stress and a plateau in the dynamic moduli. The non-linear, time dependent response was studied by using experimental protocols adapted to the study of thixotropic materials. Stepwise changes in stress or shear rate are used to monitor the kinetics of structural break-down (step-up) and build-up (stepdown). The resulting transient rheological behaviour will be critically compared to the results for weakly aggregated colloidal gels.

## Symposium EM Experimental Methods

Organizers: Anne M. Grillet and Wesley R. Burghardt

Tuesday 9:45 Room 108/109 EM1

### **Use of vibrational linear dichroism for correlating local functional group orientation to bulk stress relaxation in model acrylic polymers**

Christopher B. Walsh and Gary L. Johnson

*Corporate Research Services Department, Air Products and Chemicals, Inc., Allentown, PA 18195-1501*

Optical and spectroscopic techniques have been combined with rheological measurements by several researchers to relate microscopic functional group dynamics to macroscopic mechanical properties. This work uses polarization-modulation fourier transform infrared spectroscopy to measure the vibrational linear dichroism (VLD) signal *in situ* during stress relaxation experiments. The VLD signal is measured for several characteristic bands as a function of relaxation time and applied strain for model acrylic polymers with glass transition temperatures near room temperature, such as poly(butyl methacrylate). Differences in relaxation dynamics for main-chain and side-chain functional groups are seen in both miscible and immiscible polymer blends as well as filled homopolymer systems. These differences will be related to existing models and theories of stress relaxation.

Tuesday 10:10 Room 108/109 EM2

### **Methods for direct visualization of three-dimensional order in colloidal structures assembled by sedimentation**

Ali Mohraz, Tesfu Solomon, and Michael J. Solomon

*Department of Chemical Engineering, The University of Michigan, Ann Arbor, MI 48109*

Sedimentation is a common method for the assembly of ordered colloidal structures. Applications include photonic band gap materials and sensors. Here we report materials and methods for characterization of three-dimensional order in colloidal crystals assembled by sedimentation and visualized by confocal microscopy. The colloids are micron-size, fluorescent monodisperse poly(methyl methacrylate) dispersed in nearly refractive index matched solvents. Measures of local structure such as bond orientation parameters, vacancies and stacking faults are quantified from the confocal microscopy image volumes. We report the extension of these methods to interrogate orientational order in anisometric colloidal suspensions. Stable suspensions of nearly monodisperse fluorescent poly(methyl methacrylate) ellipsoids of variable aspect ratio (major and minor axis dimension in the range 0.5-10  $\mu$ m) have been prepared by the adaptation of literature methods. The procedure consists of the deformation of colloidal microspheres dispersed in an elastomeric matrix that is subjected to uniaxial extensional flow. The rod colloids are then retrieved from the film and dispersed in organic solvents. The centroid position and orientation angle of individual rod colloids in concentrated solution are determined by quantitative image processing. We investigate the formation of phases with orientational order in dense sediments of the highly anisometric colloids.

Tuesday 10:35 Room 108/109 EM3

### **Small angle neutron scattering under flow in the 1-2 plane: Rheo-SANS of phase-separating self-assembled wormlike surfactants and MLV formation kinetics**

Norman J. Wagner<sup>1</sup>, Matthew Liberatore<sup>1</sup>, Florian Nettesheim<sup>1</sup>, and Lionel Porcar<sup>2</sup>

<sup>1</sup>*Chemical Engineering, University of Delaware, Newark, DE 19716;* <sup>2</sup>*NIST, Gaithersburg, MD*

A new shear cell is developed and validated for making the first quantitative small angle neutron scattering measurements in the 1-2 plane (velocity-gradient) with the additional ability of resolving position within the gap. The 1-2 plane is the most interesting for studying the influence of laminar shear flow on complex fluid microstructure and this the preferred plane for rheo-optics study. There have been limited attempts to access scattering from this plane using light, x-rays and neutrons. Here, we present results obtained on a new cell design at the NCNR at NIST on NG7 that compare scattering from shear wormlike surfactant solutions in the 1-2 plane with rheo-SANS measurements taken in the 1-3 and 2-3 planes and rheo-optic measurements. Further, we apply the new cell to provide experimental resolution of two problems of significance to the nonlinear rheology of self-assembled

Tuesday Morning

surfactant solutions, namely phase separation in wormlike surfactants and the topological transitions involved in MLV formation.

Tuesday 11:00 Room 108/109

EM4

### **Particle migration patterns observed in oscillatory flow by NMRI**

Chunguang Xi and Nina C. Shapley

*Department of Chemical Engineering, Columbia University, New York, NY 10027*

Shear-induced particle migration to the center of a tube is a well-known phenomenon observed in steady, pressure-driven flows of a concentrated suspension of noncolloidal spheres in a viscous Newtonian liquid. In comparison, oscillatory, pressure-driven flow of the same material in a tube exhibits a wide range of particle distribution patterns. Observed patterns include rings and concentrated columns of particles, and appear depending on operating conditions such as bulk particle volume fraction and oscillation amplitude and frequency. Particle concentration profiles obtained by nuclear magnetic resonance imaging (NMRI) will be presented. Additional discussion will focus on determining a suitable method (NMRI or other) for quantifying the oscillation amplitude and time-dependent velocity profile in small amplitude oscillatory flow, where many of the most interesting patterns have been observed.

Tuesday 11:25 Room 108/109

EM5

### **Characterization of divergence in velocity fields during entry flow of a viscoelastic fluid by MRI velocimetry methods**

Galina E. Pavlovskaya

*Chemistry, Colorado State University, Fort Collins, CO 80523*

Magnetic Resonance Imaging (MRI) velocimetry methods have been successfully applied to characterize divergence in velocity fields occurring during fully developed flow of a viscoelastic shear-thinning fluid in an axisymmetric abrupt contraction at  $Re < 1$ . Both transverse and axial components of velocities were measured at different locations above the contraction entry plane. The area where transverse flow was detected was used to determine spatial boundaries of the divergence area. Axial velocity fields measured at different locations above the contraction entry plane were used to monitor the effect of divergence on the shape of velocity profiles. The appearance of distinctive off center maxima in axial velocity distributions was detected in the close vicinity to the entry into a 3.5:1 abrupt contraction. This usual shape of axial velocity distributions was correlated with divergent streamlines formed during entry flow of the fluid.

## **Symposium MS Entangled Melts & Solutions**

Organizers: Lynden A. Archer and Dimitris Vlassopoulos

Tuesday 9:45 Theater

MS1

### **Flow induced correlation effects within a linear chain in a polymer melt**

Roman Stepanyan<sup>1</sup>, Johan J. Slot<sup>1</sup>, Jakob Molenaar<sup>2</sup>, and Mikhail A. Tchesnokov<sup>2</sup>

<sup>1</sup>*Department of Applied Physics, University of Twente, Enschede 7500 AE, The Netherlands;* <sup>2</sup>*Department of Applied Mathematics, University of Twente, Enschede 7500 AE, The Netherlands*

A framework for a consistent description of the correlation effects along polymer chains subject to flow is proposed. The formalism shows how correlations between chain segments in the flow can be incorporated into a hierarchy of distribution functions for tangent vectors: 'n-point' probability distribution functions  $F_n$  are introduced, describing the probability that  $n$  segments along a single chain are correlated. A set of equations for the time evolution of  $F_n$  is derived for a polymer melt consisting of linear inextensible chains. The present description allows to take into account convection, retraction, reptation, (convective) constraint release, and contour length fluctuation.

Special cases of the derived set of equations (corresponding to certain closure relations for the distribution functions) are shown to yield some existing models and shed some light on the connection between them. The

simplest closure approximation yields the Doi-Edwards theory [M. Doi, S.F. Edwards, The theory of polymer dynamics] where no correlations are taken into account. A more sophisticated closure corresponds to a Milner-McLeish-Likhtman-like theory [A.E. Likhtman, S.T. Milner, T.C.B. McLeish, PRL, 85, p.4550 (2000)] for the two-point correlator. The connection between the latter and 'one-point' theories of constraint release is also discussed.

Tuesday 10:10 Theater

MS2

### **The chain retraction potential in a fixed entanglement network**

Sachin A. Shanbhag and Ronald G. Larson

*Chemical Engineering, University of Michigan, Ann Arbor, MI 48105*

When a polymer chain, pinned at one end, is immersed in a fixed entanglement network, the mobile tip of the chain encounters an entropic potential barrier that penalizes deep fluctuations needed to bring the tip close to the tethering point. Using the tube model, Doi and Kuzuu (J. Polym. Sci. C-Polym. Lett. 18, 775, 1980) estimated that this potential, which is crucial to describe the rheology of branched polymers in fixed networks and melts, has a quadratic form with a prefactor " $\nu$ " = 1.5. Later calculations based on regular lattices indicated that the potential is non-quadratic, and its steepness depends on the lattice coordination number. In this paper, we analyze the primitive-paths obtained using the bond-fluctuation model for chains with up to 12.5 entanglements. Our simulations confirm a quadratic form for the potential with a prefactor close to the Doi-Kuzuu value,  $\nu \sim 1.5$ .

Tuesday 10:35 Theater

MS3

### **Re-entanglement kinetics in sheared polybutadiene solutions**

C M. Roland<sup>1</sup>, Christopher G. Robertson<sup>2</sup>, Sandra Warren<sup>2</sup>, and Donald J. Plazek<sup>3</sup>

<sup>1</sup>Code 6120, Naval Research Laboratory, Washington, D.C. 20375-5342; <sup>2</sup>Bridgestone Americas Center for Research and Technology, Akron, OH 44317; <sup>3</sup>Dept. of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261

Interrupted shear measurements were used to follow the re-entanglement kinetics and its molecular-weight dependence for solutions of near-monodisperse polybutadiene (PB). The time-dependent recovery of the overshoot in the shear stress was measured for PB having weight average molecular weights (Mw) equal to 61, 90, 107, and 167 kg/mol, corresponding to as many as 47 entanglements per chain in solution. The times for recovery of the stress overshoot were 1.5 decades longer than the corresponding linear viscoelastic relaxation times, the latter determined from the dynamic modulus or from stress relaxation following cessation of flow. Notwithstanding the differing timescales, the Mw dependences for entanglement recovery and linear viscoelastic relaxation were equivalent (power law exponent  $\sim 3.4$ ).

Tuesday 11:00 Theater

MS4

### **Exploring nonlinear flow behavior of entangled polymers**

Prashant S. Tapadia and Shi-Qing Wang

*Department of Polymer Science, The University of Akron, Akron, OH 44325*

We have unraveled<sup>1</sup> in the past year or so that highly entangled polymer solutions undergo an abrupt constitutive bulk flow transition when imposed by a shear stress comparable to the plateau modulus  $G_N^0$ , whereas the controlled-rate experiment reveals stress leveling off around  $G_N^0$ . Key characteristics of this shear-induced entanglement-disentanglement transition have recently been disclosed.<sup>2</sup> We have carried out additional rheological and rheo-optical experiments to further explore and understand the nature of this universal flow behavior of entangled polymers.

<sup>1</sup>"Yield like constitutive transition in shear flow of entangled polymeric fluids", P. Tapadia and S.Q. Wang, *Phys. Rev. Lett.*, 91, 198301, (2003). <sup>2</sup>"Nonlinear flow behavior of entangled polymer solutions: yield like entanglement-disentanglement transition", P. Tapadia and S.Q. Wang *Macromolecules*, to be published (2004).

Tuesday Morning

Tuesday 11:25 Theater

MS5

**Interfacial and bulk healing dynamics of entangled polymer liquids at large shear stresses**

Haibo Qi and Lynden A. Archer

*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853*

We use experiment and theory to investigate an abrupt flow transition in entangled polymer liquids subject to shearing flows under controlled stress conditions. This talk focuses on the effect of interface physical chemistry and polymer microstructure on the critical stress at the transition. We also discuss the role of nucleated voids on microstructural reorganization dynamics in entangled polymer liquids sheared at stresses above the critical value.

## Tuesday Afternoon

### Symposium GP 50 Years of WLF: Glassy Polymers & Related Systems

Organizers: Sindee Simon and Ed Quitevis

Tuesday 1:50 Room 104/105

GP19

#### **Volume recovery of polystyrene**

Srinivas Kolla, Paul Bernazzani, and Sindee L. Simon

*Chemical Engineering, Texas Tech University, Lubbock, TN 79410*

A new experimental technique that uses intermittent temperature perturbations during volume recovery has been developed in order to obtain quantitative information concerning the evolution of the characteristic relaxation time for volume during structural recovery. The experiments are analogous to the intermittent creep experiments developed by Struik. Using an automated capillary dilatometer and a polystyrene sample, the time-temperature history dependence of the characteristic relaxation time for volume was investigated. Our results show that for the set of temperature down jumps and memory experiments investigated, the characteristic relaxation time depends on temperature history, as well as on the instantaneous state of the material. The results are not consistent with the TNM/KAHR model. The implications with respect to the WLF equation and free volume theory will be discussed.

Tuesday 2:15 Room 104/105

GP20

#### **Investigating environmental stress cracking using contact angle measurements**

Alan J. Lesser and Peter Walsh

*Polymer Science & Engineering Dept., University of Massachusetts, Amherst, MA 01003*

Glassy polymers exposed to certain surface-active agents may develop crazes and fail under otherwise moderate stress levels. This phenomenon is commonly referred to as environmental stress cracking or crazing (ESC). In this paper we experimentally investigate a hypothetical crazing mechanism proposed by Gent that states that the uptake of the surface active liquid into the polymer, and resulting plasticization, is stress activated. Specifically, stress induced swelling occurs because the hydrostatic tensile stress (dilatational component) increases the equilibrium volume fraction of surface active liquid in the polymer. The liquid molecules are generally small enough that the volume they displace can be considered equivalent to added free volume in the glassy polymer. At some critical hydrostatic stress the free volume increases enough that the polymer transitions from a glassy to a rubbery state. Gent further proposes that asperities at the polymer surface lead to local stress concentrations which become preferential sites for localized swelling and subsequent craze initiation. This paper probes this hypothesis for initiation using contact angle measurements. The system chosen for study is polycarbonate with oleic acid. An experimental technique involving contact angle measurements of a sessile drop as a function of stress is presented. A novel technique for contact angle measurements using refraction is also introduced.

Tuesday 2:40 Room 104/105

GP21

**Determination of WLF constants for a food polymer system: Effect of water activity and degree of crosslinking**

Jozef L. Kokini<sup>1</sup>, Mustafa E. Yildiz<sup>2</sup>, and Bharani Ashokan<sup>1</sup>

<sup>1</sup>*Department of Food Science, Rutgers University, New Brunswick, NJ 08854;* <sup>2</sup>*Princeton University, Princeton, NJ*

The Williams, Landel and Ferry (WLF) equation is useful in predicting the temperature-induced changes in foods near the glass transition temperature. Knowledge of the WLF constants, which are known to be material properties rather than 'universal values', and their variability, is essential to predict mobility based properties such as diffusion coefficients which help to predict changes in quality during shelf life of foods. Adequate information on the magnitude of the WLF constants as a function of polymeric property changes during processing and storage is not available in the food literature.

In this research, we investigated the WLF properties of defatted soy flour as a function of storage conditions and processing parameters. The effect of storage conditions on the magnitude of WLF constants was estimated by conducting dynamic mechanical spectroscopic measurements on soy flour dough samples stored at various water activities. The influence of processing parameters on the WLF constants of defatted soy flour was determined by cooking or extruding the soy at various temperatures to induce varying degrees of crosslinking. The WLF constants were estimated using shift factors that were obtained with the time-temperature superposition principle.

The WLF constants for extruded soy flour were found to be different from the universal values reported for synthetic polymers and show variations across differing water activities and cooking temperatures. An increase in the water activity manifested itself as a decrease in the glass transition temperature of the sample. A suitable correlation was found between this change in glass transition and the observed variation in the WLF constants. An increase in the degree of crosslinking showed an increase in the WLF constants which was attributed to a decrease in the free volume in the sample. In conclusion, WLF constants for soy flour were shown to be material specific and different from the "universal values".

Tuesday 3:05 Room 104/105

GP22

**Controlled Epoxy network structure-property relationships: Effect of chain termination and host crosslink density**

Nikhil E. Verghese<sup>1</sup>, Maurice J. Marks<sup>1</sup>, Anamari Laboy-Torro<sup>2</sup>, and Ha Q. Pham<sup>1</sup>

<sup>1</sup>*Thermosets Product R&D, The Dow Chemical Company, Freeport, TX 77541;* <sup>2</sup>*Chemical Engineering and Material Science, University of Minnesota, Minneapolis, MN 55455*

While epoxy thermosets are commonly used and are best known for their high glass transition temperature (T<sub>g</sub>), creep resistance, environmental resistance and high stiffness, they are extremely complicated and intractable to thorough investigation. This is in part due to the fact that these are curing systems and gelation marks a turning point in the system's performance as well as ability to be probed for effective structure-property relationships. In addition, practical formulations often contain multiple components that have subtle but important interactions to the final performance.

In this presentation we will cover work that was performed recently to quantitatively probe the effect of one such practical yet important effect, namely chain termination. The effect of the size as well as flexibility of the chain termination group will be examined via a controlled host matrix chemistry that comprises of DER<sup>TM</sup>332 resin as the epoxy, bisphenol A as extender and tris(4-hydroxyphenyl)ethane (THPE) as a crosslinker. In addition the effect of crosslink density of this thermoset on chain termination will also be studied. Data and trends pertaining to T<sub>g</sub>, stiffness, yield strength, fracture toughness and thermal expansion coefficient will be discussed.

## Symposium RM Rheology at Microscopic Scale

Organizers: Shelley L. Anna and Anubhav Tripathi

Tuesday 3:55 Room 104/105

RM1

### **Polymer films at the air/water interface: Rheology and simulation**

Grant T. Gavranovic<sup>1</sup>, Joshua M. Deutsch<sup>2</sup>, and Gerald Fuller<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Stanford University, Stanford, CA 94305*; <sup>2</sup>*Physics, University of California, Santa Cruz, Santa Cruz, CA 95064*

Some amphiphilic polymers can be confined at the air/water interface to form essentially-2D systems, and these structures can be considered as analogs to 3D polymer solutions and melts. In this study, the rheological properties of monolayers of the flexible polymer poly(*tert*-butyl methacrylate) (PtBMA) were examined, and computer simulations were used to investigate the nature of similar 2D polymer systems.

For PtBMA molecular weights between 80,000 and 780,000 g/mol, surface pressure vs. area isotherms were measured, as were surface shear viscoelastic properties. Using an interfacial stress rheometer, the surface storage and loss moduli were determined over a range of frequencies. Creep compliance experiments were also performed to elucidate the dependences of surface shear viscosity on surface pressure and polymer molecular weight. Additionally, changes in the rheological properties of PtBMA monolayers with varying surface pressure were related to phase transitions observed during compression isotherms.

Computer simulation experiments of 2D polymer systems similar to the PtBMA films studied physically have shown the effects of such parameters as polymer-surface attraction and polymer-polymer attraction on surface pressure and other equilibrium film properties. These simulations have been beneficial in understanding molecular-level polymer conformation in confined geometries.

Tuesday 4:20 Room 104/105

RM2

### **Influence of elasticity on the dynamic interface shapes of polymer melts and Boger fluids**

Gitanjali K. Seevaratnam<sup>1</sup>, Steve Garoff<sup>2</sup>, and Lynn M. Walker<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213*; <sup>2</sup>*Physics Department, Carnegie Mellon University, Pittsburgh, PA 15213*

In this work, we characterize the liquid-vapor interface shape during forced wetting to quantify the effect of fluid elasticity on interface shape. The fluid mechanics near the three phase (solid-liquid-vapor) are complex and the impact of elasticity on this inherently confined geometry is poorly understood. We find that two polymer melts, PIB and PS exhibit dynamic wetting characteristics of a weakly elastic fluid. We study dynamic wetting by observing the liquid-vapor interface formed on the outside of a silica surface forced into a bath of the test fluid at controlled rates. The results show that the interface shapes of these fluids deviate from the prediction of models that include only Newtonian flow behavior. This observation is surprising as elasticity is not detected for these materials using standard rotational rheometry. Experiments on xanthan gum solutions which exhibit shear thinning dominated rheology have shown that an increase in shear thinning decreases the curvature of the interface near a moving contact line. To validate our argument we observe the interface shape of an analogous model Boger fluid having elasticity dominated rheology and show that elasticity causes similar, although in larger magnitude, deviations from Newtonian behavior. The conclusion of this study is that these viscous polymer melts are non-Newtonian and that the interface shape shows deviations from the Newtonian model caused even by weak elasticity in fluids.

Tuesday 4:45 Room 104/105

RM3

### **Formation of Newtonian and polymeric drops via shear-dominated flows in microchannels**

Aaron J. Greiner<sup>1</sup>, Gordon F. Christopher<sup>2</sup>, Joshua A. Taylor<sup>2</sup>, and Shelley L. Anna<sup>2</sup>

<sup>1</sup>*Michigan State University, Lansing, MI*; <sup>2</sup>*Carnegie Mellon University, Pittsburgh, PA*

Microfluidic devices have recently been demonstrated as an effective method of generating monodisperse drops and bubbles on a drop-by-drop basis. In this talk we focus on shear-dominated flows in microfluidic devices, in which

drops of an aqueous liquid form in a T-shaped geometry due to shearing of a second oil phase. We compare the drop formation mechanism and the ultimate drop sizes for Newtonian drops and drops made of a constant viscosity elastic polymer solution, where the shear viscosities of the two liquids are matched. We characterize the drop formation mechanism and the resulting drop size over a large number of experiments by varying capillary number, volume fraction, and viscosity ratio. We observe at least two distinct modes of breakup that depend on these three dimensionless parameters. In the first mode, drops shear off near the t-junction, and the drop size decreases with increasing capillary number. The second mode resembles jet breakup via a capillary instability, and here drop sizes are nearly independent of capillary number. We observe that polymer drops are not significantly different in size from Newtonian drops formed under the same conditions. In addition, polymer drops form by nearly the same mechanism as Newtonian drops, except that stable liquid threads persist between drops, dramatically increasing breakup times.

## **Symposium SC Suspensions and Colloids**

Organizers: Jan Vermant and Dan Klingenberg

Tuesday 1:50 Room 107

SC10

### **Laser tweezer microrheology of colloidal suspensions**

Eric M. Furst, John P. Pantina, Myung-han Lee, and Alexander Meyer

*Department of Chemical Engineering, University of Delaware, Newark, DE*

The micromanipulation and dynamical capabilities of laser tweezers provide the ability to probe the mechanics and interactions of colloidal materials at nanometer to micrometer lengthscales. We will present a recent application of laser tweezers to investigate the mechanical properties of colloidal aggregates. This approach enables us to bridge macroscopic rheology of colloidal gels to the underlying microstructural response, and furthermore, provides critical insight into the nanoscale near-contact interactions between particles. Second, we will demonstrate adaptations of these methods to study the microrheology of suspensions by trapping single probe particles in a dense bath of fluorescent, refractive index-matched particles. Microrheology is performed simultaneously with video-rate confocal imaging, making possible direct measurements of microscopic response functions. This is of particular interest towards understanding the dynamics and rheology of colloidal glasses and gels.

Tuesday 2:15 Room 107

SC11

### **Measuring the critical stress to breakup aggregates of carbon nanotubes using microfluidic traps**

Paul R. Start, Steven D. Hudson, Erik K. Hobbie, and Kalman Migler

*Polymers Division, NIST, Gaithersburg, MD 20899*

The critical stress to break aggregates of multiwalled-carbon nanotubes suspended in low-molecular-weight polyisobutylene has been measured in planar elongational flow, produced in a microfluidic device. Through image analysis of aggregates and their fragments, the extension rate of the flow and the size and aspect ratio of the aggregates are measured in real time. While trapping an aggregate at the stagnation point of the planar elongational flow, the flow rate is continually increased, and breaking events are recorded, establishing a correlation of aggregate size and stress. In turn, the number of tubes within an aggregate, estimated from fractal geometry, is approximately proportional to stress<sup>-0.66</sup>. We compare these measurements with clustering and breakup data in simple shear.

Tuesday 2:40 Room 107

SC12

**Probing frequency dependence of fluid structure in a nano-particle suspension**Yong Zheng<sup>1</sup>, Daniel De Kee<sup>1</sup>, and Xuefeng Wang<sup>2</sup><sup>1</sup>*Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118;* <sup>2</sup>*Mathematics, Tulane University, New Orleans, LA 70118*

This paper investigates the effects of oscillatory frequency on the structural parameter of a thixotropic material. The material is composed of alumina in acetic acid. The size of the particles is around 30 nm. These small particles can agglomerate to form large particles. From dynamic experimental results, we have obtained the frequency hysteresis in  $\tan\delta$ , the evolution of  $\tan\delta$  as a function of oscillation cycles, and the effect of frequency on the magnitude of the evolution of  $\tan\delta$ . A single structural parameter model, based on the concept of effective crosslink sites, is shown to be able to describe these experimental observations.

Tuesday 3:05 Room 107

SC13

**Application of Nth-nearest neighbor statistics to characterize clustering in melt-cast composite materials**Jeremy W. Leggoe*Chemical Engineering, Texas Tech University, Lubbock, TX 79410*

Spatial heterogeneity in the distribution of the introduced phase can exert a profound influence on the macroscopic properties of composite materials. Spatial heterogeneity is typically induced during material synthesis, with interdendritic segregation of the introduced phase being a particular problem for melt cast composites. Local matrix variations, combined with the prevalence of failure nucleation sites and the complex stress states arising within particle clusters, can adversely influence the fracture properties of polymer and metal matrix composites. Characterizing the nature of spatial heterogeneity is essential to the development of computational simulations that realistically recreate spatially heterogeneous composites. A variety of measures of disorder or heterogeneity have been developed that compare the short-range characteristics of particle distributions with those of random particle dispersions, such as nearest neighbor statistics or Pair-Distribution functions. Care must be taken, however, that such measures are based on comparisons with appropriate dispersions; particle dispersions are not Poisson point processes, and polydispersity can substantially influence nearest neighbor statistics. This investigation is developing Nth nearest neighbor statistics as a tool for characterizing the extent and length scale of clustering in particulate reinforced materials. Consideration is given to the influence of the form in which the particle distribution is characterized on the data collected; 2D microstructure representations can yield statistics varying significantly from the those obtained for the actual three dimensional structure. The development of physically based forms of heterogeneous spatial distribution recreation, such as the placement of repulsive nodes to generate three dimensional "necklaced" particle structures representative of interdendritic segregation, will also be discussed in this presentation

Tuesday 3:55 Room 107

SC14

**Viscoelasticity of suspensions of Xanthan gum gel fragments**George B. Thurston*Dept. of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78746*

The use of suspensions of gel fragments having controlled dimensions, deformability and aggregation tendencies offers a new prospect for mobility control in enhanced oil recovery by injection in porous structure. Rheological properties of Xanthan gum gel fragments in suspensions are determined, both in large tubes where bulk properties dominate and in small spaces of a porous structure where the gel fragments choke the passage ways. The suspensions are prepared from Xanthan gum solutions gelled by Cr(3+) as cross-linking agent. Then the gels are fragmented by chopping with a high speed rotating blade. The bulk rheology is described by the frequency dependence of the viscoelasticity at low shear rates and the oscillatory shear dependence of the viscoelasticity at a fixed frequency. This is done for the original Xanthan gum solution prior to gelation, the fully formed gel, the fragmented gel, and suspensions of gel fragments. The kinetics of re-gelation (aggregation of the gel fragments) is described. The flow of the suspensions through porous media, showing fragment trapping in the pores, is demonstrated.

Tuesday 4:20 Room 107

SC15

**Magnetic emulsions with tunable stability**

Sonia Melle<sup>1</sup>, Mauricio Lask<sup>2</sup>, and Gerald Fuller<sup>2</sup>

<sup>1</sup>*Departamento de Óptica, Ciudad Universitaria, Madrid, Madrid 28040, Spain;* <sup>2</sup>*Chemical Engineering, Stanford University, Stanford, CA 94305*

We prepare solid-stabilized emulsions using paramagnetic particles at an oil/water interface that can undergo macroscopic phase separation upon application of an external magnetic field. A critical field strength is found for which emulsion droplets begin to translate into the continuous-phase fluid. At higher fields, the emulsions destabilize, leading to a fully phase-separated system. This effect is reversible and long-term stability can be recovered by remixing the components with mechanical agitation.

Tuesday 4:45 Room 107

SC16

**Transient rheology and structure evolution in ER and MR suspensions**

Daniel J. Klingenberg<sup>1</sup>, Joachim Hoerrmann<sup>1</sup>, David Kittipoomwong<sup>1</sup>, Yannis Pappas<sup>1</sup>, John C. Ulicny<sup>2</sup>, and Jeffrey F. Morris<sup>3</sup>

<sup>1</sup>*Chemical and Biological Engineering, University of Wisconsin, Madison, WI;* <sup>2</sup>*Materials and Processes Lab, General Motors, Warren, MI;* <sup>3</sup>*Energy Services Group, Research, Halliburton, Houston, TX 77032*

Electro- and magnetorheological (ER and MR) suspensions are well known for their changes in rheological properties when external electric or magnetic fields, respectively, are applied. The ability to rapidly and reversibly control the apparent suspension viscosity over orders of magnitude has been exploited in the development various torque transfer and semi-active damping devices. Some applications have recently been commercialized.

One of the major challenges in the development of certain applications is that the rapid increase in suspension viscosity caused by the application of an external field is typically followed by a slow, transient evolution of the viscosity. The viscosity can continue to increase for minutes to hours, depending on the flow conditions. Experiments and particle-level simulations suggest that this transient evolution of the apparent rheological properties is associated with the formation and coarsening of lamellar structures within the fluid.

In this presentation, we will review the experimental and simulation evidence for lamellar pattern formation and the transient evolution of the rheological properties of ER and MR suspensions. We will then discuss the mechanisms that control the slow coarsening of these structures, as well as the mechanisms by which the pattern formation alters the rheological properties. We will also describe a continuum model for the long-time evolution of the lamellar structures, and compare predictions with our experimental observations.

Tuesday 5:10 Room 107

SC17

**Flow based control of conductivity in nanotube suspensions**

Sam Kharchenko, Jan Obrzut, Jack Douglas, and Kalman Migler

*Polymers Division, NIST, Gaithersburg, MD 20899*

Nanotube composites are finding applications due to their ability to enhance the electrical conductivity of polymeric materials. The flow fields generated during the processing of the non-Brownian suspensions of multi-wall nanotube suspensions in a molten polymer matrix (polypropylene) are critical in producing the final electrical properties. These fluids exhibit a percolation threshold in both rheological and electrical properties at nanotube concentrations of ~1/2 % by mass. We study the interrelationship between these two coupled transport properties by simultaneous dielectric spectroscopy and rheology. We find that the DC electrical conductivity is quite sensitive to shear flow near the percolation threshold; it can decrease by five orders of magnitude and can become highly anisotropic upon application of a shear rate on the order of 5 s<sup>-1</sup>. Examining the frequency dependence of the conductivity, we observe that steady shear flow can change the material from a conductor to an insulator. Further, we find that the conductivity recovers upon cessation of shear. Interestingly, the shear dependence of the viscosity and the conductivity show distinct behaviors, indicating that different aspects of the nanotube network are probed when measuring these two transport coefficients.

## Symposium EM Experimental Methods

Organizers: Anne M. Grillet and Wesley R. Burghardt

Tuesday 1:50 Room 108/109

EM6

### **A new rheometer with unprecedented low torque performance**

Bernard A. Costello, Nigel R. Doe, Peter W. Foster, and Raoul E. Smith

*TA Instruments Ltd, Crawley RH10 9NB, United Kingdom*

TA Instruments announce the launch of a new rheometer with many new features. In this presentation we will describe mainly the improvements that have been made in the low torque performance. New technologies have been used to provide low torque performance substantially better than that previously obtainable on commercial rotational rheometers. This improvement has been made through a complete redesign of the instrument motor and bearing, to reduce their contributions to the instrument friction and residual torque, without compromising on the instrument inertia or its axial, lateral or torsional compliances. The motor redesign has also allowed major advances to be made in the instrument response times and its direct strain control.

In this presentation we will show the instrument performance in the absence of sample, and for a series of materials such as decane, which has a viscosity of 0.92 mPa.s, and various low viscosity standard oils, in steady shear and dynamic modes. We will also show how this leads to better quality data for materials of greater rheological interest, allowing access to parts of the material performance space previously unavailable to the experimentalist.

Tuesday 2:15 Room 108/109

EM7

### **A novel nanobubble method for measuring the creep compliance of ultrathin polymer films**

Paul A. O'Connell and Gregory B. McKenna

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

There has been a surge of interest in the properties of polymers on the nano-scale. Many researchers have observed a reduction in the glass temperature of free standing films by as much as 70K below 40 nm in thickness. Much of the past work in thin polymer films has been performed in a pseudo-thermodynamic mode where a change in the slope of a property with temperature is interpreted as the glass temperature. Mechanical measurements, such as nano-indentation of an AFM tip, have also been carried out. However, such studies are difficult to interpret due to contact mechanics issues. We have developed a novel nano-mechanical measurement technique that allows the determination of the biaxial creep compliance of ultrathin polymer films. We have scaled the classic bubble inflation technique so that films of nanometer thickness can be tested. An important aspect of this technique is that it uses the imaging capability of the AFM to perform the deformation measurements - thus bypassing the contact mechanics issues mentioned above when the AFM is used as a nano-indentation machine. In the test, a thin polymer film is deposited over a silicon filter containing an array of through holes with a diameter of 1.2 microns. Placing a pressure gradient across the membrane causes the material over the holes to inflate. The inflated membrane takes on a hemispherical shape and the AFM is used to measure the bubble profile. For a viscoelastic material the bubble shape can be followed over time and the creep compliance function determined. We present here results on the measurement of the creep compliance of poly (vinyl acetate) (PVAc) and polystyrene (PS) at thicknesses down to approximately 30 nm. Results from PVAc suggest that in the segmental relaxation regime the material behaves in a bulk-like fashion at 30nm thickness, with no indication of a reduction in T<sub>g</sub>. The PS shows a moderately reduced T<sub>g</sub> at film thicknesses below 70 nm. A surprisingly large reduction in the plateau compliance is also observed and will be discussed.

Tuesday 2:40 Room 108/109

EM8

**A study of dynamic heterogeneity in polymers by mechanical spectral hole burning (MSHB)**

Xiangfu Shi and Gregory B. McKenna

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

Non-resonant spectral hole burning (NSHB) has proven to be a powerful tool for the investigation of heterogeneous dynamics in glass forming materials. We have previously shown that the types of material non-linearities represented by typical nonlinear viscoelastic constitutive models cannot fully or consistently reproduce the observed hole-burning behaviors, which is consistent with the response being due to dynamic heterogeneity. Here we have constructed a Mechanical Spectral Hole Burning scheme (MSHB), analogous to Dielectric Spectral Hole Burning (DSHB). We have performed the first mechanical hole burning experiments on two polymeric systems: a low density polyethylene (LDPE) melt and a polystyrene/diethyl phthalate solution. Unlike the NSHB dielectric experiments, here we examine dynamics in the terminal relaxation regime. In the hole burning experiment the material is subjected to a large sinusoidal "pump" followed by a small step "probe" in either a positive or a negative direction. The difference between the positive and negative probes in a linear system gives the linear response, e.g., the relaxation modulus in MSHB. The experimental results for the two polymeric systems studied here show distinguishable and systematic mechanical holes. The hole positions and intensities were investigated as a function of pump frequency, pump amplitude and waiting time (hole-refill). Mechanical holes, which are similar to those obtained in the DSHB studies, indicate a non-uniform modification to the linear response. These findings provide evidence for the existence of heterogeneous relaxation dynamics for entangled polymeric systems in the reptation or terminal regime. The studies suggest that MSHB is a novel tool for the study of dynamic heterogeneity in the generally low dielectric constant polymeric systems. It also demonstrates that MSHB may be a powerful tool for the study of the nonlinear viscoelastic behavior of polymers.

Tuesday 3:05 Room 108/109

EM9

**A new real time measurement of the true gap size during parallel-plate and cone-and-plate rheological testing**

Joerg Laeuger<sup>1</sup>, Patrick Heyer<sup>1</sup>, and Gerhard Raffer<sup>2</sup>

<sup>1</sup>*Product Management, Anton Paar Germany GmbH, Ostfildern D-73760, Germany;* <sup>2</sup>*Anton Paar, Graz, Austria*

The actual size of the measuring gap in rotational rheometers has been a matter of discussions for a long time. An error in the gap size influences directly the measuring results in parallel-plate and cone-and-plate measurements. In modern rheometer the length change of the measurements systems due to thermal expansion is taken into account by using gap correction routines. However, these adjustments are based on fixed expansion coefficients which do not describe transient behavior during temperature ramps and due to changing laboratory conditions.

In order to overcome the limitations of existing gap adjustment procedures a patented method (US Patent 6,499,336) which directly measures the actual gap size during the running experiments is introduced. The measuring principle is based on an induction method. Since it does not require any mechanical interaction with the sample the rheological experiment will not be influenced by the gap measurement at all. Unlike in existing methods, the new device does not approximate the gap size, but, directly measures and keeps constant the real gap size during the running experiment.

The developed real gap measurements device is working over an extended temperature range. It can be incorporated into Peltier, electrical resistance, and convection based environmental systems, respectively. Measurements of the temperature distribution within the gap show that the new device does not have any negative impact on the uniformity of the temperature distribution within the gap.

## Symposium SA Self-Assembled & Associating Fluids

Organizers: Srinivasa R. Raghavan and Yenny Christanti

Tuesday 3:55 Room 108/109

SA1

### **Correlations between rheology and molecular structure for telechelic associative polymers**

Xiaoxia Meng<sup>1</sup> and William B. Russel<sup>2</sup>

<sup>1</sup>National Starch & Chemical Co, Bridgewater, NJ 08807; <sup>2</sup>Graduate School, Princeton University, Princeton, NJ 08544

We combine predictions of the high frequency modulus with correlations for the relaxation time to estimate the low shear viscosity of the telechelic associative polymers consisting of PEO backbones end capped with hydrophobes in aqueous solutions. Our approach recognizes that the polymers aggregate to form spherical micelles, whose aggregation number and radius determines the rheology. The aggregation number is determined by the balance of the interfacial energy against the energy of stretching the end blocks to form the core, the configurational entropy, and excluded volume interactions of the soluble chains in the corona. The minimum in the free energy sets the most probable size, while the curvature at the minimum indicates the breadth of the distribution and the radius follows through Li-Witten's model for spherical brushes(1). The high frequency modulus is computed from the pair interaction potential in the pair interaction limit (2), while a correlation for the relaxation time is constructed from experimental data (3). Low shear viscosity follows from the product of the high frequency modulus and the relaxation time.

Comparison of our predictions with data from the literature and our own experiments with model associative polymers demonstrate consistent agreement, given a constant correction factor in the modulus to account for hydrodynamic interactions. Comparison with commercial polymers with slightly different chemical structures suggests fundamental differences and reflects the sensitive of the response to the molecular structure. Thus we offer the first model that recognizes the micellar structure of these solutions and offers reasonable predictions of the rheology.

1. Li, H. and Witten, T. A., *Macromolecules* 1994, 27, 449-457. 2. Zwanzig, R.; Mountain, R.D. *J. Chem. Phys.* 1962, 43, 4464. 3. Annable, T.; Buscall, R.; Ettelaie, R.; Whittelstone, D. J. *Rheol.* 1993, 37, 695-726

Tuesday 4:20 Room 108/109

SA2

### **Variation of hydrophobic interactions in nonionic surfactant/associative polymer systems**

Sachin Talwar, Lauriane F. Scanu, and Saad A. Khan

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

The rheological behavior of hydrophobically modified associative polymer solutions in the presence of nonionic surfactants is investigated. Such polymer-surfactant systems are usually used to control the rheology of water-borne coatings. Hydrophobically modified alkali-soluble emulsion (HASE) polymers are comb-like associative polymers with pendant hydrophobes that form a network in an alkaline solution consisting of both intra- and intermolecular hydrophobic junctions. The addition of surfactant affects the dynamics of these solutions by forming free as well as bound micelles incorporating the polymer hydrophobes. The nonionic surfactants used in our study are nonylphenol polyethoxylates (NP) with different ethylene oxide (EO) chain lengths, which determine the hydrophilic-lipophilic balance (HLB) of the surfactant. The effects of temperature, surfactant EO chain length, and polymer and surfactant concentrations on the rheology of the polymer-surfactant systems are studied. Steady shear and dynamic experiments are performed and the trends of zero shear viscosity and longest relaxation time are examined. Arrhenius plots are used to determine the strength of the hydrophobic junctions. Results show that the zero shear viscosity exhibits a maximum at low surfactant concentrations and then decreases to a plateau value lower than the pure polymer viscosity with increasing surfactant concentration. This behavior is independent of the temperature or the polymer concentration. The observance of a maximum in viscosity at low surfactant concentration is consistent with results on similar HASE polymer with anionic surfactants and with nonionic surfactants of higher HLB but has not been observed previously with intermediate HLB nonionic surfactants. Variation of the longest relaxation time

Tuesday Afternoon

and the strength of the hydrophobic junctions follow the same trend as the viscosity with increasing surfactant concentration. These results are interpreted in terms of formation of mixed junction domains.

Tuesday 4:45 Room 108/109

SA3

**Rheometric estimation of binding constant for cyclodextrin-hydrophobe complexation in associative polymers**

Shamsheer Mahammad and Saad A. Khan

*Department chemical and biomolecular engineering, North Carolina State University, Raleigh, NC 27695*

We develop a new rheometric method to estimate the binding constant for cyclodextrin-hydrophobe complexation in hydrophobically modified associative polymer solutions. The associative polymers form a transient network due to intermolecular hydrophobic interactions. This network can be disrupted by encapsulation of hydrophobes within the cyclodextrin (CD) cavity that results in reduction of the viscoelastic properties of the polymer solution by several orders of magnitude. It is found that not all the added CD participate in the complexation, but there exists a dynamic equilibrium between the CD adsorbed to the hydrophobes and free CD in solution. We develop a rheology based Langmuir type adsorption isotherm to estimate the binding constant for the molecular complexation. The model is based on the assumption that each CD adsorbed encapsulates a network junction and hence reduces dynamic moduli. The dynamic frequency sweep spectrum is fit to a generalized Maxwell model and the network junction density is estimated using transient network theory. The effects of temperature on binding constant are studied to estimate the enthalpy and entropy and free-energy of complexation. The study is carried out with both a and b CD at different polymer concentrations. The complexation with a-CD presents higher equilibrium constant and free energy change indicating stronger adsorption of CD to hydrophobes compared to that of b-CD. The polymer concentration also affects the binding constant and other thermodynamic parameters due to increase in net effective junction density.

Tuesday 5:10 Room 108/109

SA4

**pH-triggered release of polycation-b-poly(ethylene glycol) from liposomes**

Debra T. Auguste<sup>1</sup>, Robert K. Prud'homme<sup>1</sup>, Timothy Deming<sup>2</sup>, Steven Armes<sup>3</sup>, and Joachin Kohn<sup>4</sup>

<sup>1</sup>*Chemical Engineering, Princeton University, Princeton, NJ 08544;* <sup>2</sup>*Materials Science and Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106-5050;* <sup>3</sup>*Department of Chemistry, University of Sussex, Brighton, BN1 9QJ, United Kingdom;* <sup>4</sup>*Chemistry, Rutgers University, Piscataway, NJ 08854-8058*

The ability to protect liposomes is critical for DNA gene therapy applications. We present research on electrostatic protection and deprotection of liposomes by pH sensitive anchoring of PEG-polycationic polymers. Controlled release of adsorbed polymers from liposomes allows synergy between protection (from immune recognition) and intracellular delivery of DNA. Polycationic polymers, poly(dimethylaminoethyl methacrylate) (0.8, 3.1, 4.9, or 9.8 kg/mol) or polylysine (3 kg/mol), act as anchors for poly(ethylene oxide) (2 or 5 kg/mol). In addition, a comb-graft copolymer with 15 repeating blocks of PEO (2 kg/mol) bound to an amine, was evaluated as a protective coating. Incorporation of 1,2-dioleoyl-3-dimethylammonium-propane, a titratable lipid, allows the liposome's net charge to shift with pH, resulting in decreased polymer adsorption. Polymer adsorption exceeds calculated values for liposome neutralization, resulting in adsorption profiles in the brush regime.

## Symposium MS Entangled Melts & Solutions

Organizers: Lynden A. Archer and Dimitris Vlassopoulos

Tuesday 1:50 Theater

MS6

### **Origin of super soft states in bulk polymers**

Tadeusz Pakula

*Max Planck Institute for Polymer Research, Mainz 55021, Germany*

Creating new macromolecular architectures can constitute a challenge for synthetic chemists but can additionally be justified if it can result in new properties of materials. Mechanical properties, which are related to the dynamics of systems with various complex macromolecular structures will be discussed. Bounding monomeric units to linear polymer chains creates dramatically different material properties. Whereas, a monomer in bulk can usually be only liquid-like or solid (e.g. glassy), the polymer can additionally exhibit a rubbery state with properties, which make these materials extraordinary for a large number of applications. The rubbery state of the polymer extends between the segmental (monomer) and the chain relaxations and is controlled by a number of parameters related to the polymer structure. In the rubbery state the material is much softer than in the solid state. If expressed by the real part of the modulus, the typical solid state elasticity is of the order of 10<sup>9</sup> Pa and higher, whereas, the rubber-like elasticity in bulk polymers is typically of the order of 10<sup>5</sup>-10<sup>6</sup> Pa. It will be demonstrated that some highly branched macromolecular structures can lead to considerably different properties than these obtained by linking monomeric units into linear chains. The examples consider dynamic behavior of multiarm stars in the melt, the melts of brush-like macromolecules and hairy micelles dispersed in linear polymer matrices. In all these systems, there exists a third relaxation process with the longest relaxation time, which is interpreted as related to slow cooperative rearrangements in the structured system. When slow enough, it can create a new elastic plateau with the plateau modulus (10<sup>2</sup>-10<sup>3</sup> Pa) by orders of magnitude lower than characteristic for the conventional polymeric rubbery state. We have recently observed such super soft elasticity in a number of systems, including block copolymers which can be considered as super soft thermoplastic elastomers.

Tuesday 2:15 Theater

MS7

### **A molecular model for slip at polymer melt/solid interfaces**

Mikhail A. Tchesnokov<sup>1</sup>, Jakob Molenaar<sup>1</sup>, Johan J. Slot<sup>2</sup>, and Roman Stepanyan<sup>2</sup>

<sup>1</sup>*Department of Applied Mathematics, University of Twente, Enschede 7500 AE, The Netherlands;*

<sup>2</sup>*Department of Applied Physics, University of Twente, Enschede 7500 AE, The Netherlands*

A molecular model for wall slip is developed which unifies two slip mechanisms into a single framework. Desorption and disentanglement are taken into account self-consistently, so that the model can be applied over a wide range of adhesive energies, including those where both slip mechanisms occur in parallel. The proposed model is quantitative and allows to quantify the stick-slip transition in terms of the geometry, molecular and surface parameters. A complex non-monotonic temperature and wall material dependence is found for the critical shear stress and shear rate which can be used to figure out the dominant slip mechanism in a real experiment. It is found that adhesive failure occurs only on low energy surfaces such as fluoroelastomer, and that on high-energy surfaces such as steel, polymer melts usually slip cohesively, by the sliding of polymer over a strongly adsorbed wall layer. Since in many real experiments the value of the adhesive energy is rather high, only slip due to disentanglement can be considered. The model predictions show a good agreement with experimental data over a wide range of adhesive energies and temperatures.

Tuesday 2:40 Theater

MS8

**Affect of interfacial slip on polymer/polymer adhesion**

Phillip J. Cole, Jianbin Zhang, and Christopher W. Macosko

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

Zhao and Macosko (J. Rheology 2002, 46, 145) reported interfacial slip between immiscible polymers under high stress. We have found decreased adhesion between coextruded polymer layers when the wall shear stress exceeds the level where interfacial slip is expected to be significant. Polystyrene/poly(methyl methacrylate) coextrudates showed nearly a three fold decrease in adhesion at high flow rates. Full interfacial strength recovered rapidly upon static annealing. The effect of flow on reactive coupling of chains in the interface and resulting adhesion was also investigated.

Tuesday 3:55 Theater

MS10

**On the modeling of the Rheotens experiment for polymer melts with kinetic theory constitutive viscoelastic equations**

Antonios K. Doufas<sup>1</sup>, Irina Graf<sup>1</sup>, and Marc Mangnus<sup>2</sup>

<sup>1</sup>Core R&D, Dow Chemical Company, Freeport, TX 77541; <sup>2</sup>Plastics R&D, Dow Benelux B.V., Terneuzen, The Netherlands

A fundamental model for the rheotens experiment is developed by coupling the transport equations of the process with non-linear viscoelastic constitutive equations based on polymer kinetic theory. The very good fitting and predictive capability of the model will be discussed for a variety of Dow's polyolefin-based resins and processing conditions. The model is a useful tool for determination of an apparent elongational viscosity vs. strain rate flow curve of polymer melts from rheotens data.

Tuesday 4:20 Theater

MS11

**A critical study of high-rate uniaxial extensional melt flow and the melt fracture behavior of linear polyethylenes**

Martin L. Sentmanat<sup>1</sup>, Edward Muliawan<sup>2</sup>, and Savvas Hatzikiriakos<sup>2</sup>

<sup>1</sup>Senkhar Technologies, LLC, Akron, OH 44303; <sup>2</sup>The University of British Columbia, Vancouver, British Columbia, Canada

The melt fracture and extensional flow behaviors of a series of linear polyethylenes were characterized from capillary extrusion and uniaxial extension melt rheology experiments. Based on the experimental results it was determined that the critical shear rates for the onset of both sharkskin and gross melt fractures were found to correlate with the high-rate extensional flow behavior of the polymer melts. These findings were found to mechanistically support the generally accepted observations of melt fracture phenomena occurring at the exit (sharkskin) and entrance (gross) regions of the capillary die. In addition, it was found that the presence of a small amount of boron nitride (BN) filler behaves as an energy dissipater that suppresses the rapid increase of extensional stress associated with gross melt fracture, and enables the BN to act as an effective processing aid in postponing the onset of gross melt fracture.

Tuesday 4:45 Theater

MS12

**Chain dynamics in linear polymer melts: A neutron spin echo study**

Andreas Wischniewski<sup>1</sup>, M Zamponi<sup>1</sup>, M Monkenbusch<sup>1</sup>, L Willner<sup>1</sup>, Dieter Richter<sup>1</sup>, Alexei Likhtman<sup>2</sup>, Tom McLeish<sup>2</sup>, B Farago<sup>3</sup>, and G Kali<sup>3</sup>

<sup>1</sup>Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Juelich 52425, Germany; <sup>2</sup>Department of Physics, University of Leeds, Leeds, United Kingdom; <sup>3</sup>Institut Laue Langevin, Grenoble, France

We report on a direct experimental determination of the time dependent mean squared displacement of a polymer segment in the melt covering the transition from free Rouse relaxation to constraint motion along the virtual tube of the reptation model. This has been achieved by a NSE measurement of the segmental self-correlation function. While this experiment supports the concept of topological confinement in long chain polymer systems, as described in the

tube model, a close comparison of linear rheology data with predictions of the reptation model indicates the existence of additional degrees of freedom that release the topological confinement. As one candidate, fluctuating chain ends escaping the tube confinement starting from both ends were proposed. In order to study this mechanism on a microscopic scale, we have measured the single chain dynamic structure factor by NSE spectroscopy on polyethylene melts over a large range of chain lengths. While at high molecular weight the reptation model is again corroborated, a systematic loosening of the confinement with decreasing chain length is found. The dynamic structure factors are quantitatively described by taking into account the effect of contour length fluctuations (CLF). Partly labeled chains allow to separate CLF from the reptation process. By a comparison of their dynamic structure factor with fully labeled chains the CLF process was identified unambiguously. A second relaxation process which has been incriminated to limit the topological confinement in polymer melts is the relaxation of the tube itself. First measurements of a long test-chain with fixed length in different matrix molecular weights allow to observe the loosening of confinement with decreasing molecular weight of the matrix. However, a scattering function which could describe this constraint release effect quantitatively is still not available.

Tuesday 5:10 Theater

MS13

**Tube dilation and reptation in binary blends of monodisperse linear polymers**

Seung Joon Park<sup>1</sup> and Ronald G. Larson<sup>2</sup>

<sup>1</sup>*LG Chem, Ltd, Daejeon 104-1, Republic of Korea;* <sup>2</sup>*Chemical Engineering, University of Michigan, Ann Arbor, MI 48109*

Reptation of the long chain in binary blends of monodisperse linear 1,4-polybutadienes and 1,4-polyisoprenes is tested using linear viscoelastic rheology measurements for two blends with different values of the "Graessley parameter"  $Gr = M_2 \cdot M_e^2 / M_1^3$ , where  $M_1$  is the short-chain molecular weight,  $M_2$  is the long-chain molecular weight, and  $M_e$  is the entanglement molecular weight. For polybutadiene and polyisoprene blends in which  $Gr$  is smaller than the critical value  $Gr_c = 0.064$  established by an observed cross-over in diffusivity measurements (Green et al. Phys. Rev. Lett. 1984, 26, 2145), the long-chain motion in the binary blend is well predicted by the Milner-McLeish model using reptation in the undiluted tube, and a dilution exponent of unity. However, for  $Gr$  larger than  $Gr_c$ , reptation must to be assumed to occur in a dilated tube to obtain agreement with the experimental data. These results confirm that the cross-over behavior observed in diffusivity also occurs in rheology, and show that existing tube models can accurately predict linear rheology in both regimes where reptation occurs in a dilated or an undiluted tube.



# Wednesday Morning

## Symposium PL Plenary Lectures

Wednesday 8:30 Theater

PL3

### **Rheology and microrheology of composite actin networks**

David Weitz

*Harvard University, Cambridge, MA*

Actin is a protein that is ubiquitous in cells. It polymerizes to form long, rigid filaments, whose aspect ratio can be of order 1000. In cells, it polymerizes to form a rigid network, which forms the basis of the cellular cytoskeleton, providing important mechanical rigidity to the cell. An essential component of this network are additional actin binding proteins, which help control and regulate the cytoskeleton. This talk will describe the remarkable elastic behavior of actin networks formed in the presence of actin binding proteins, and will show that the behavior is well described by a robust model that allows quantitative predictions of the elasticity. It will show the essential role played by the binding proteins, not only in the linear modulus, but also in the elastic properties observed for large strain. Results from both macro and microrheology will be described, providing new insight into the origin of the elastic behavior.

## Symposium RM Rheology at Microscopic Scale

Organizers: Shelley L. Anna and Anubhav Tripathi

Wednesday 9:45 Room 104/105

RM4

### **Single particle motion in colloidal dispersions as a model for nonlinear microrheology**

John F. Brady<sup>1</sup>, Aditya S. Khair<sup>1</sup>, Ileana Carpen<sup>1</sup>, and Todd M. Squires<sup>2</sup>

<sup>1</sup>*Chemical Engineering, California Institute of Technology, Pasadena, CA 91125*; <sup>2</sup>*Applied and Computational Mathematics and Physics, California Institute of Technology, Pasadena, CA*

Over the last decade or so a set of experimental procedures collectively known as 'microrheology' has emerged as an intriguing alternative to traditional 'macrorheology' techniques, with the ability to probe the viscoelastic properties of soft heterogeneous materials (e.g. polymer solutions, colloidal dispersions, biomaterials) at the micrometer scale. One of the most popular microrheology techniques involves the tracking of a single particle to infer properties of the embedding material. One may perform a passive tracking experiment where the change in particle location due to random thermal fluctuations of the surrounding medium is monitored and used to infer the linear viscoelastic nature of the surrounding environment. In contrast, active tracking experiments in which the system is driven out of equilibrium by application of an external force on the probe particle may be used to study the nonlinear viscoelastic properties of materials. Much less work has been conducted on active microrheology as compared to its passive counterpart. As a model for active microrheology we consider the motion of a single Brownian probe particle under the imposition of a steady external force amidst a sea of force-free colloidal particles. The non-equilibrium spatio-temporal configuration or microstructure of particles induced by the motion of the probe is calculated and used to infer the dispersion's 'effective microviscosity'. The computed effective viscosity is in good agreement with previous macrorheology studies of sheared suspensions. Results from Brownian Dynamics simulations of this process are also discussed. This work suggests that active tracking microrheology can be a valuable tool with which to explore the rich nonlinear rheology of complex materials.

Wednesday 10:10 Room 104/105

RM5

**Probing the microstructure of Carbopol using multiple particle tracking and dynamic light scattering**Felix Oppong<sup>1</sup>, Laurent Rubatat<sup>2</sup>, Barbara J. Frisken<sup>2</sup>, Arthur E. Bailey<sup>2</sup>, and John R. de Bruyn<sup>1</sup><sup>1</sup>*Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada;* <sup>2</sup>*Department of Physics, Simon Fraser University, Burnaby, BC V5A 1S6, Canada*

We study the microstructure of dispersions of Carbopol ETD 2050 in water using video fluorescence microscopy to track the motion of small tracer particles. The mean square displacement of the particles can be described by a power law in time. The diffusive exponent  $\alpha$  is equal to one for low carbopol concentrations, indicating normal diffusion. At moderate concentrations  $\alpha$  is between zero and one, indicating subdiffusion as the structure of the fluid constrains the particle motion. At high concentrations (of order 1%),  $\alpha$  is close to zero. At this concentration the carbopol is a stiff gel and the particles are almost completely confined. The distribution of particle displacements is Gaussian at low concentrations but deviates from Gaussian as the concentration is increased, when it is better described by the sum of two Gaussians, one for a subset of the particles that move relatively freely and the other for a more constrained subset. From correlations between successive particle displacements, we estimate the length scale of the fluid microstructure. Quasi-elastic light scattering from tracer particles was used to provide complementary measurements of diffusion and viscoelastic properties on shorter length and time scales. These results are in very good agreement with the microscopy data. In contrast, we find substantial differences between our microscale measurements and the results of conventional shear rheometry.

Wednesday 10:35 Room 104/105

RM6

**Microbead rheology of lung mucus: Experiments and modeling**Greg Forest<sup>1</sup>, David Hill<sup>2</sup>, Lingxing Yao<sup>1</sup>, and Richard Superfine<sup>2</sup><sup>1</sup>*Applied Mathematics, Institute for Advanced Materials, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250;* <sup>2</sup>*Physics and Astronomy, UNC, Chapel Hill, NC 27599*

Experimental protocols of a distribution of bead sizes in laboratory cultures of mucus, representative of healthy and diseased samples, will be described. The linear viscoelastic properties are inferred from the theory of Mason and Weitz. We then test the self consistency of the theory with microscopic-macroscopic modeling, with the goal to turn the underpinnings of microbead rheology on its head, so to speak, to predict the mean square displacement data of pathogens in biological liquids. This strategy is motivated by medical applications for modeling bacterial infections or drug therapies.

Wednesday 11:00 Room 104/105

RM7

**Analysis of the embedment of nanospheres into polymer surfaces: Is there a liquid layer?**Stephen A. Hutcheson and Gregory B. McKenna*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

There is considerable interest in the rheological response of polymeric materials both at the nano-scale and at surfaces. One reason for this is the observation that the glass temperature of free-standing films can be reduced by over 70 K [1] upon reduction of the film thickness to below 40 nm. One hypothesis about the cause of the reduction of the glass temperature in thin films is that there is a surface liquid layer that propagates into the bulk of the film. Here we examine quantitatively measurements performed by Teichroeb and Forrest [2] in which colloidal gold (Au) particles were placed onto the surface of a polystyrene (PS) film and their rate of embedding into the surface was followed with an AFM. The results were interpreted to show the existence of a liquid surface layer. We use the Ting [3] viscoelastic contact mechanics model and include the surface interactions between the PS and the Au particles to calculate the creep compliance of the material based on the reported embedding data. From the bulk creep compliance data for PS [4] we calculated the  $h(t)$  vs.  $t$  curve for all test temperatures below the bulk  $T_g$  of PS. We find that the data agree with the calculations shifted to a temperature of 373 K, which is 5 K above the 368 K temperature of the test. Similar calculations and comparison with the data reveal results that are not consistent with the existence of a surface liquid layer if one considers that the reported  $T_g$  reductions in extremely thin films can be as great as 70 K. Experiments to replicate those of Teichroeb et al [2] are in progress.

References: 1. K. Dalnoki-Veress, J.A. Forrest, C. Murray, C. Gigault and J.R. Dutcher, *Phys. Rev. E.*, 63, 031801 (2001) 2. J.H. Teichroeb and J.A. Forrest, *Phys. Rev. Lett.*, 91, 016104 (2003). 3. T. C. T. Ting, *Journal of Applied Mechanics*, 33, *Trans. ASME*, 66, Series E, 438-444, (1966). 4. D.J. Plazek and V.M. ORourke, as cited by J.D. Ferry, *Viscoelastic Properties of Polymer*, 3rd ed., Wiley, New York, 1980, p. 605.

Wednesday 11:25 Room 104/105

RM8

### **Scaling laws for polymers using mesoscopic simulations**

Vasileios Symeonidis<sup>1</sup>, Bruce Caswell<sup>2</sup>, and George E. Karniadakis<sup>1</sup>

<sup>1</sup>*Division of Applied Mathematics, Brown University, Providence, RI 02912;* <sup>2</sup>*Division of Engineering, Brown University, Providence, RI 02912*

Bead-spring representations of chains are used as the polymer model in simulations of dilute solutions by dissipative particle dynamics (DPD). Three combinations of forces, representing different bond types, are used. For two model cases, in addition to the elastic forces between neighbors each bead is the center of a Lennard-Jones potential which interacts with all other beads. The complex process of detecting phantom collisions is avoided by use of an indicator which reports the number of bond-length exceedences beyond the critical value necessary for a bead to pass through the chain. The static exponent scaling law is used to measure success in the avoidance of phantom collisions. Small values of the indicator were found to correlate with powers close to 3/5, the Flory value for self-avoiding walks. Large indicator values are associated with powers near to 1/2, the value for ideal random walks. Chain behavior under steady shear shows no similar scaling law but different stretching response for finitely and infinitely extensible springs. The effect of temperature is also investigated for a fixed number of monomers.

## **Symposium SC Suspensions and Colloids**

Organizers: Jan Vermant and Dan Klingenberg

Wednesday 9:45 Room 107

SC18

### **Transient response of the electrical conductivity of suspensions upon a reversal in the direction of shear**

Ely R. Greenberg and Francis A. Gadala-Maria

*Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208*

The effect of a reversal in the direction of shear on the transient rheological properties (shear stress and normal stress differences) of non-colloidal suspensions has been reported in the past. This work reports the effect of a reversal in the direction of shear on the transient electrical properties of suspensions. Shearing was found to have a significant effect on the electrical conductivity of suspensions of graphite particles in a non-conductive resin. The transient electrical conductivity measured upon the start of shear was found to depend on the direction in which the suspension was previously sheared. In a similar fashion to the effect on the rheological properties, the transitions in the electrical conductivity upon reversal of the direction of shear correlate to the strain on the suspension (rather than to the shear rate or time separately). Surprisingly, the effect of shear on electrical conductivity is very different at moderate concentrations (near 30 wt %) than at high concentrations (near 50 wt %) of graphite. The results may have applications to the manufacture of the electrically conductive composite materials, and the technique may provide an additional tool for the study of the interactions between particles in suspensions.

Wednesday 10:10 Room 107

SC19

### **Anisotropy of sheared carbon nanotube suspensions**

Erik K. Hobbie<sup>1</sup>, Dan Fry<sup>1</sup>, and Hao Wang<sup>2</sup>

<sup>1</sup>*NIST, Gaithersburg, MD;* <sup>2</sup>*Michigan Technological University, Houghton, MI*

We measure the anisotropy of sheared carbon nanotube suspensions for a broad range of concentration, aspect ratio, and strain rate using a variety of methods. Our measurements highlight the importance of hydrodynamic excluded-volume interactions in the semi-dilute regime, with scaling in terms of a dimensionless shear rate, or Peclet number.

Our results also suggest that such interactions might be exploited to fractionate carbon nanotubes by length in simple shear flow.

Wednesday 10:35 Room 107

SC20

### **Effects of fiber shape on the rheology of fiber suspensions**

Emilio J. Tozzi<sup>1</sup>, C. T. Scott<sup>2</sup>, and Daniel J. Klingenberg<sup>1</sup>

<sup>1</sup>*Chemical and Biological Engineering, University of Wisconsin, Madison, WI 53706;* <sup>2</sup>*USDA Forest Products Laboratory, Madison, WI 53706*

Fiber-level simulations are employed to determine the effects of fiber shape on the rheological properties of fiber suspensions in shear flow. For fixed fiber aspect ratio, the suspension viscosity is larger for suspensions composed of non-straight fibers than for suspensions of straight fibers. The increase in suspension viscosity arises from several mechanisms, each associated with the fact that non-straight fibers tend to tumble with a shorter period. Fiber shape has previously been characterized by such quantities as the fiber curl index (related to the fiber contour length divided by the end-to-end distance) and the kink index (related to the distribution of sharp bends in the fiber). We show that these measures of fiber shape do not correlate well with the suspension viscosity. Alternate measures of fiber shape based on the eigenvalues of the fiber mass moment tensor and the hydrodynamic resistance tensors correlate much better with the suspension viscosity. The amenability of these various measures to experimental measurement will also be discussed.

Wednesday 11:00 Room 107

SC21

### **Dilute rheology of functionalized SWNTs (*f*-SWNTs) in strong acids**

Pradeep K. Rai<sup>1</sup>, Nicholas G. Parra-Vasquez<sup>1</sup>, Virginia A. Davis<sup>1</sup>, Robert A. Pinnick<sup>1</sup>, Anil K. Sadana<sup>2</sup>, Jayanta Chattopadhyay<sup>2</sup>, Feng Liang<sup>2</sup>, Ed Billups<sup>2</sup>, Robert H. Hauge<sup>3</sup>, Richard E. Smalley<sup>3</sup>, and Matteo Pasquali<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, Rice University, Houston, TX 77005;* <sup>2</sup>*Department of Chemistry, Rice University, Houston, TX 77005;* <sup>3</sup>*Rice University, Houston, TX*

The manipulation and processing of single-wall carbon nanotubes (SWNTs) is limited by their insolubility in most common solvents. The strong van der Waals interactions between SWNTs as they are synthesized results in the formation of bundles of tubes, called "ropes", which are not easily broken up into individual tubes by either temperature or by solvents. Covalent sidewall functionalization of SWNTs provides an excellent route to solubilize the nanotubes in common solvents.

We are studying the relationship between sidewall functionalization, and phase behavior of solutions of *f*-SWNTs in strong acids. We have used polarized light microscopy to visualize the dispersions of functionalized tubes. Butylated SWNTs and 9-Nonadecynated SWNTs are well dissolved in 102% sulfuric acid. Viscosity measurements in dilute solutions are sensitive to de-bundling achieved in the solution. We compare the viscosity-concentration dependence of dilute pristine and *f*-SWNTs to assess whether and how functionalization promotes de-bundling and stabilizes the tubes, and to determine the average length of *f*-SWNTs. Change in either phase behavior or viscosity versus concentration dependence is expected to result in differences in fiber spinning processability. Alternatively, adding sulfate salts to dispersions of pristine SWNTs in 96% and 102% H<sub>2</sub>SO<sub>4</sub> improves solubility by inducing electrostatic repulsion between SWNTs.

Wednesday 11:25 Room 107

SC22

### **Alignment and orientation effects of particles suspended in viscoelastic fluids**

Jan L. Vermant, Deniz Gunez, Rossella Scirocco, and Jan Mewis

*Department of Chemical Engineering, K.U. Leuven, Leuven B-3001, Belgium*

When particles are suspended in viscoelastic fluid rather than in Newtonian liquids, the dynamics and particle orientations observed during flow will be dramatically altered. The hydrodynamic forces exerted onto the particles by the fluid are affected by features such as shear thinning and the occurrence of normal stress differences. As a consequence, it is well known that spherical particles display alignment phenomena of particles ordering into strings at volume fractions where the suspensions in a Newtonian counterpart are well into a dilute regime. However, this alignment has been shown to depend in a subtle manner on the rheological features of the suspending fluid. For non-

spherical particles, were particles spin in Jeffery orbits in Newtonian liquids, the particles can develop preferred orientations in either flow or the vorticity direction when suspended in viscoelastic liquids. The dynamics of the particle orientation are studied by means of rheo-optical methods. In suspensions containing non-spherical particles, string formation is no longer observed.

## Symposium SA Self-Assembled & Associating Fluids

Organizers: Srinivasa R. Raghavan and Yenny Christanti

Wednesday 9:45 Room 108/109

SA5

### **Tuning the linear viscoelastic behavior of wormlike micelles**

Michael J. Gerber<sup>1</sup>, MyHang T. Truong<sup>2</sup>, and Lynn M. Walker<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213;* <sup>2</sup>*Physical & Analytical Science, Lubrizol Corporation, Wickliffe, OH 44092*

We are characterizing the influence of additives on the rheology of wormlike solutions of cationic surfactant. The effect of hydrotropic counterion, nonionic polymer and competitive counterion on the linear viscoelastic behavior has been quantified. Conclusions about the influence of these additives on micellar structure are drawn through the use of existing rheological models and direct measurement (using small angle light and neutron scattering). All of this work focuses on the cationic surfactant cetyltrimethylammonium (CTA<sup>+</sup>). By varying the length of these slow-breaking micelles (defined in the context of the theory developed by Cates) and their degree of entanglement, mixed systems offer more precise control of the rheology than available in pure CTA<sup>+</sup> systems. As an example, nonionic macromolecular additives are used to tune the linear viscoelastic behavior of aqueous semidilute wormlike micellar systems of cetyltrimethylammonium p-toluenesulfonate (CTAT). Polyethylene oxide (PEO) enhances the terminal viscosity of the CTAT system, while the number of entanglements per micelle remains constant. Increasing the concentration of CTAT also has the same effect on the viscosity, but the degree of entanglement increases dramatically. Through binding and comicellization, hydroxypropylcellulose (HPC) and block copolymers of ethylene oxide and propylene oxide (Pluronic copolymers) cause the formation of shorter micelles. As such, these mixed systems have lower viscosities and degrees of entanglements, yet the viscoelastic behavior remains qualitatively similar to the original CTAT system. The interactions of these polymers with CTAT allow for modifications of the micellar structure without changing the volume fraction of micelles, thus creating rheological behavior, which cannot be achieved in pure CTAT systems. Similar trends and behaviors are noted in systems with different counterions and ionic additives and will be discussed.

Wednesday 10:10 Room 108/109

SA6

### **Development of a solvent/temperature superposition for a solution of rod-like micelles**

Phillip Sullivan<sup>1</sup>, Robert K. Prud'homme<sup>2</sup>, and Wanwipa Siriawatwechakul<sup>2</sup>

<sup>1</sup>*Schlumberger, Sugar Land, TX 77478;* <sup>2</sup>*Chemical Engineering, Princeton University, Princeton, NJ 08544*

Solutions of rod-like micelles formed from visco-elastic surfactants have found increasing use in industrial applications such as district heating and oil and gas production. In these applications, rheological properties are of interest over a broad temperature range, and experimental measurements are desired at elevated temperatures where laboratory measurements are inconvenient or technically difficult to perform. A recent investigation of the effects of an organic solvent on the scission energy of rodlike micelles formed from erucyl bis(hydroxyethyl) methylammonium chloride suggests that a "solvent/temperature" superposition can be developed for a solution of rodlike micelles. In this superposition the rod contour length and dynamics ( $G'$  and  $G''$ ) at elevated temperature can be simulated at ambient temperature by the appropriate addition of an organic solvent such as ethanol. The ability to quantitatively prescribe solvent conditions to match elevated temperature conditions follows from a theoretical model for the structure and dynamics of rod-like micelle fluids. This superposition technique affords a convenient and rational way of performing room temperature experiments to simulate high temperature behavior that is otherwise very difficult to explore.

Wednesday 10:35 Room 108/109

SA7

**Fluctuations and order in wormlike micelles under shear**

Paul T. Callaghan<sup>1</sup>, M R. Lopez-Gonzalez<sup>1</sup>, William M. Holmes<sup>1</sup>, and P J. Photinos<sup>2</sup>

<sup>1</sup>*MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington, New Zealand;* <sup>2</sup>*Department of Physics, University of Southern Oregon, Ashland, OR*

Using rapid NMR velocimetry and NMR spectroscopy we demonstrate the existence of shear band fluctuations in the Couette flow of the wormlike micelle system, 10 % w/v cetylpyridinium chloride/sodium salicylate (molar ratio 2:1) in 0.5 M NaCl brine. We show that the fluctuations may be either quasi-random or periodic, the fluctuation spectrum being similar to that observed in the stress. Despite the equilibrium fluid being far from an isotropic-nematic transition, deuterium NMR shows that the onset of shear banding is associated with a nematic micellar state whose order parameter is close to unity and depends on shear rate. The behaviour observed tends to support a recent model by Fielding and Olmsted in which hydrodynamic properties are coupled to micellar chain length.

Wednesday 11:00 Room 108/109

SA8

**Viscosity increase with temperature caused by a vesicle to wormlike micelle transition**

Tanner S. Davies, David M. Griffin, and Srinivasa R. Raghavan

*Department of Chemical Engineering, University of Maryland, College Park, MD 20742*

Complex fluids based on surfactants usually show a decrease in their viscosity upon heating. We report an instance where the opposite effect occurs, i.e., there is a sharp increase in viscosity over a range of temperatures. The system of interest is a mixture of the cationic surfactant, cetyl trimethylammonium bromide (CTAB) and an alkyl-substituted salicylic acid. This mixture self-assembles in aqueous solution to form unilamellar vesicles at room temperature. When the solution is heated, the vesicles progressively transform into long, cylindrical micelles or "wormlike" micelles. In the process, the solution is transformed from a low-viscosity, Newtonian fluid into a viscoelastic, shear-thinning fluid with a much higher zero-shear viscosity (factor of 1000 larger). At higher temperatures, the contour length of the wormlike micelles is reduced and the viscosity decreases. Thus, the viscosity shows a maximum as a function of temperature. The ensuing microstructural changes as a function of temperature are confirmed by small-angle neutron scattering (SANS) measurements. We will discuss and correlate the rheology and SANS data for various sample compositions.

Wednesday 11:25 Room 108/109

SA9

**Nanoparticle dynamics in solutions of wormlike micelles**

Matthew Liberatore, Florian Nettesheim, Eric W. Kaler, and Norman J. Wagner

*Chemical Engineering, University of Delaware, Newark, DE 19716*

Some surfactant molecules in solution self-assemble into wormlike micelles. Solutions of wormlike micelles behave similarly to polymers, but in addition are able to reversibly break and recombine. Suspensions of small particles (~1 to 1000 nanometers in size) in micellar solutions are common in the cosmetic, detergent and food industries. The phase behavior of cationic nanoparticles (< 100 nanometers in diameter) in a cationic micellar solution will be explored at various temperatures as a function of particle and salt concentration. In general, surface tension measurements provide evidence that the surfactant does not adsorb onto the particles. The variable of interest is the ratio of the particle size to the micelle mesh size. Investigations of particle motion within the micelle network by several scattering techniques, including static light scattering and small-angle neutron scattering, will be described. Additionally, rheological measurements under steady and dynamic flows will be compared to micellar solutions without suspended particles. Rheo-optical studies (i.e., birefringence and dichroism) near the phase boundaries demonstrate shear-induced phase separation and/or shear banding.

## Symposium MS Entangled Melts & Solutions

Organizers: Lynden A. Archer and Dimitris Vlassopoulos

Wednesday 9:45 Theater

MS14

### **Prediction of linear viscoelastic properties for polydisperse mixtures of entangled star and linear polymers : Modified tube-based model and comparison with experimental results**

Evelyne van Ruymbeke<sup>1</sup>, Roland Keunings<sup>1</sup>, and Christian Bailly<sup>2</sup>

<sup>1</sup>*CESAME & POLY, Universite catholique de Louvain, Louvain-la-Neuve, Belgium;* <sup>2</sup>*POLY, Universite catholique de Louvain, Louvain-la-Neuve, Belgium*

We have developed and tested a new model suitable for the prediction of linear viscoelasticity from knowledge of molecular structure for arbitrary mixtures of (asymmetric) star and linear entangled molecules. The model is very general and contains the key ingredients of tube models: reptation, fluctuations, "influence of the environment" constraint release and tube dilation. Reptation and fluctuations in the potential are treated in a classical way. However, we impose no artificial time scale separation between the fluctuations and reptation processes but rather treat both as simultaneous and progressive. Early fluctuations are treated in a new way, simple but effective, based on a potential vs. thermal energy level criterion. Because the systems modelled can be arbitrary mixtures, there can be no analytical solution and a time-marching algorithm has to be used. At each time step, the key parameters to be calculated are the reptation and fluctuations times of each segment. To this end, the interrelations between fluctuations and reptation processes have to be taken into account very carefully through the inclusion or exclusion of the constraint release solvent in the considered relaxation process. We have come to the conclusion that a generalization of the concept of "Graessley number", that is the ratio of a characteristic constraint release time over a characteristic relaxation time, can be used as a criterion for the decision to include or exclude the solvent and thus to consider the skinny of the dilated tube for the relaxation process. The model has been tested on a wide range of literature data pertaining to polybutadiene, polyisoprene and polystyrene model systems, leading to excellent quality predictions, provided that the constraint release solvent is correctly treated. In particular, we do not need to impose artificial simplifications (reptation as time-step process) or ad hoc parameter modifications for asymmetric stars to get good predictions.

Wednesday 10:10 Theater

MS15

### **Evaluation of a new constitutive equation for mixtures of entangled linear polymers and application to the study LAOS polystyrene melts**

Adrien Leygue<sup>1</sup>, Chen-Yang Liu<sup>2</sup>, Nicolas Coppin<sup>2</sup>, Henri Burhin<sup>3</sup>, Christian Bailly<sup>2</sup>, and Roland Keunings<sup>1</sup>

<sup>1</sup>*CESAME, Universite catholique de Louvain, Louvain-la-Neuve, Belgium;* <sup>2</sup>*POLY, Universite catholique de Louvain, Louvain-la-Neuve, Belgium;* <sup>3</sup>*Alpha Technologies, Louvain-la-Neuve, Belgium*

In this work, we present and evaluate a new constitutive equation for blends of entangled linear polymers. The model is built on a tensorial expression for a full chain representation of the microstructure. Reptation and stretch relaxation mechanisms are accounted for, while both thermal and convective constraint release are introduced in a unified formulation. The model is named CRAFT chain model (Constraint Release Average Tensorial Full Chain Model). Due to the connectivity of the tube segments, the resulting constitutive equation has the form of a set of coupled partial differential equations along the tube coordinate. The numerical predictions of the model are computed using a finite difference discretisation of those coupled equations, leading to a coupled multimode system. The new formulation of constraint release can be extended to the case of polydisperse systems to provide a mixing rule which, in the linear regime, is equivalent to the mixing rule of double reptation. With the help of the model, we study the transient response of an entangled polymer melt subject to a large amplitude oscillatory shear flow (LAOS). The possibility to control both the maximum shear rate and the maximum deformation allows one to better differentiate the influence of Weissenberg from Deborah numbers on material response. LAOS experiments therefore provide a tough test for non-linear constitutive equations. Through the comparison of experiments with the predictions of the model, we try to connect qualitative features of the time and frequency responses to molecular

parameters describing the samples. A particular emphasis is put on the polymer chains stretch dynamics and on the molecular weight distribution of the samples.

Wednesday 10:35 Theater

MS16

### **The composition dependence of viscosity in miscible polymer blends**

Timothy P. Lodge and Jeffrey C. Haley

*Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455*

There is significant interest in the prediction of the composition-dependent rheological properties of binary polymer mixtures. In particular, considerable attention has been paid to the composition dependence of miscible blend viscosities. Through a combination of the Lodge-McLeish model for segmental dynamics, and the double reptation model for the chain dynamics, reasonable predictions of miscible blend viscosities are possible, with no adjustable parameters. In this contribution, we present new comparisons of predictions with viscosity measurements for model blend systems. The results suggest that some outstanding issues remain. A modified constraint release model is used to make improved predictions of blend component relaxation times. Preliminary results indicate that this approach is able to resolve at least some of the discrepancies between measured and predicted viscosities in molecular weight blends.

Wednesday 11:00 Theater

MS17

### **Evaluation of different methods for the determination of the plateau modulus $G_N^0$ and the entanglement molecular weight $M_e$**

Chen-Yang Liu<sup>1</sup>, Evelyne van Ruymbeke<sup>2</sup>, Adrien Leygue<sup>2</sup>, Roland Keunings<sup>2</sup>, and Christian Bailly<sup>1</sup>

<sup>1</sup>*POLY, Universite catholique de Louvain, Louvain-la-Neuve, Belgium;* <sup>2</sup>*CESAME, Universite catholique de Louvain, Louvain-la-Neuve, Belgium*

Recently Larson et al. [1] carefully reviewed and clarified the different definitions of entanglement spacing and time constants in tube models. However, the precise experimental determination of the plateau modulus  $G_N^0$  and the entanglement molecular weight  $M_e$  has not received enough attention in literature and large discrepancies between published values are found for important polymers such as polyethylene and polycarbonate. In this study, we compare and assess the accuracy of published methods as well as possible experimental errors, by analyzing the dynamic moduli of a wide range of polymers, including monodisperse model polymers and polydisperse commercial polymers or polymer mixtures. The plateau modulus values, obtained by a fitting procedure of tube model parameters minimizing discrepancy with experimental data are also compared with the above results. For long-chain linear model polymers ( $M_w/M_n > 20$ ), such as polybutadiene, polyisoprene and polystyrene, there is satisfactory agreement (within 10 %) between the various methods. The weak dependence of  $G_N^0$  or  $G''_{max}$  on molecular weight as  $Z_e^{0.1-0.15}$ , predicted by Likhtman and McLeish [2], is not observed in the range  $Z_e = 10$  to 500. Polydispersity causes a big uncertainty for the evaluation of the plateau modulus, especially for some semi-crystalline polymers and condensation polymers, which are difficult to obtain as high  $M_w$  and narrow MWD samples. Due to the low molecular weight part in polydisperse polymers, it is difficult to correctly resolve the terminal behavior from the transition and Rouse regions. Two methods to resolve the  $G''$  terminal region are discussed for these systems. Finally, branched polymers have a much broader terminal relaxation spectrum, which obscures the estimate of the plateau modulus.

[1] RG Larson et al., J. Rheol. 2003,47, 809-818.

[2] AE Likhtman and TCB McLeish, Macromolecules 2002,35, 6332-6343.

Wednesday 11:25 Theater

MS18

**Rheology of architecturally complex polymer melts**Michael Kapnistos<sup>1</sup>, Dimitris Vlassopoulos<sup>1</sup>, Jacques Roovers<sup>2</sup>, Nikos Hadjichristidis<sup>3</sup>, and Gary Leal<sup>4</sup>

<sup>1</sup>*Institute of Electronic Structure & Laser, FORTH, Heraklion, Crete 71110, Greece;* <sup>2</sup>*Institute for National Measurement Standards, NRC, Ottawa, Ontario, Canada;* <sup>3</sup>*Department of Chemistry, University of Athens, Athens, Greece;* <sup>4</sup>*Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA*

We report on the linear rheological properties of entangled polymers with architectural complexity. In particular, we present dynamic mechanical data of a series of well defined linear combs, star combs, Caley-tree-like polymers with different chemistries (polystyrene, polybutadiene, polyisoprene). Based on the tube model theories, we analyse their linear response and shed light into their relaxation mechanisms. We modify the model to take into account architectural details that affect their relaxation mechanisms, as well as their polydispersity. The latter matters a great deal, even if its nominal value is small, and is accounted for by explicitly considering Schulz-Zimm distributions for the size polydispersity of arms, backbones and branching number. The model, which describes the data well, contains no adjustable parameters and the values of physical quantities are determined from the chemical characterization or the rheological experiments. Our findings indicate that the concept of hierarchical motions provides the proper framework for describing the physical mechanisms that govern the relaxation of such complex macromolecules. Some remaining open questions are also addressed.



# Wednesday Afternoon

## Symposium RM Rheology at Microscopic Scale

Organizers: Shelley L. Anna and Anubhav Tripathi

Wednesday 1:50 Room 104/105

RM9

### **Extensional flow of dilute polymer solutions through microfabricated hyperbolic contractions**

Monica S. N. Oliveira, Lucy E. Rodd, and Gareth H. McKinley

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

This study focus on the characterization of the extensional flow of dilute solutions of high molecular weight polymer through planar hyperbolic contractions. The set of converging geometries are designed to produce constant extensional rates along the centerplane and to yield different values of the total Hencky strain from 1 to 3.7. The polydimethylsiloxane (PDMS) microchannels are fabricated from a chrome mask using soft-lithography techniques, thus permitting tight control of the spatial features, with a minimum feature size of  $10\mu\text{m}$ . Aqueous solutions of polyethylene oxide (PEO;  $M_w = 2,000,000$  g/mol) with a range of concentrations from 500 to 3000 ppm (spanning the dilute and semi-dilute regimes) are employed as the working fluids. The flow in the contraction region is analyzed by means of streak photography, video microscopy and microscopic digital particle image velocimetry ( $\mu\text{PIV}$ ).

The configurations studied here allow for the examination of flows at low to moderate Reynolds numbers and high Deborah numbers. Strong viscoelastic effects are observed, even for dilute solutions, as a consequence of the small length scales and high deformation rates associated with the microchannel flow. The pressure drop across the hyperbolic contractions is also measured to enable the computation of an apparent planar extensional viscosity for deformation rates in the range  $100 - 12,000$   $\text{s}^{-1}$ . The development of vortices at moderately high Reynolds numbers is also observed, and the competing effects of inertia and elasticity on the flow structure are discussed.

Wednesday 2:15 Room 104/105

RM10

### **Dynamics of wormlike micelles in extensional flows**

Philip A. Stone<sup>1</sup>, Paul Dalhaimer<sup>2</sup>, Dennis E. Discher<sup>2</sup>, Eric J. Amis<sup>1</sup>, Steven D. Hudson<sup>1</sup>, and Kalman Migler<sup>1</sup>

<sup>1</sup>*Polymers Division, NIST, Gaithersburg, MD 20899-8542;* <sup>2</sup>*Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA*

Micelles and vesicles formed of amphiphilic diblock copolymers, often called 'polymersomes', may have applications in drug delivery and in understanding the physics of biological structures. Wormlike micelles, in particular, provide an opportunity to study the behavior of semiflexible rods in extensional flows. We utilize microfluidic devices coupled with fluorescence microscopy to study the dynamics of wormlike micelles formed of amphiphilic diblock copolymers. Individual micelles are imaged in a planar extensional flow generated by a simple cross-flow device with dimensions of the order of 100 microns. Over a wide range of stress, controlled by the solvent viscosity and the extensional rate, we measure micellar stretch and orientation on the micrometer scale and map out the transition from coil to stretch behavior.

Wednesday 2:40 Room 104/105

RM11

**Microfluidic rheometry using flow-induced birefringence**

Jai A. Pathak and Steven D. Hudson

*Polymers Division, NIST, Gaithersburg, MD 20899-8544*

The rheological characterization of complex fluids in micro-scale flows is an important scientific and technical challenge in microfluidics. Towards a goal to integrate synthesis of model polymers with their physical and rheological characterization on a lab-on-a-chip platform, we present quantitative measurements of flow-induced birefringence in complex fluids undergoing planar elongational flow, and other mixed flows, produced in microchannels that function analogously to a four-roll mill. Upon carefully applying the stress-optical rule for systems where it is known to work, we use birefringence data to measure stress differences and planar elongational viscosities of polymer solutions and wormlike micellar surfactant solutions (in the latter, the stress-optical rule works over a narrow range of deformation rates).

Wednesday 3:05 Room 104/105

RM12

**Rheological study of fluid flow in microchannels subjected to uniform injection and suction**

Mohammad Layeghi

*Mechanical Engineering, Sharif University of Technology, Tehran, Tehran 11365-9567, Iran*

Analytical analysis of fluid flow in cylindrical microchannels subjected to uniform wall injection and suction at various Reynolds numbers is presented. The classical Navier-Stokes equations are used in the present study. Mathematically, using an appropriate change of variable, Navier-Stokes equations are transformed to a set of nonlinear ordinary differential equations. The governing equations are solved analytically using series solution method. The presented analytical results can be used for the prediction of velocity profiles and pressure drops in the cylindrical micro channels. The results are validated against available data in the literature and have shown good agreement.

Wednesday 3:55 Room 104/105

RM13

**Chaotic mixing in a microfluidic device driven by oscillatory electroosmotic flow**

Frederick R. Phelan Jr., Jai A. Pathak, and Jan Obrzut

*Polymers Division, NIST, Gaithersburg, MD 20899*

Chaotic mixing in a microfluidic device is studied by both modeling and experimentation. The device consists of an oscillatory, cross-channel mixing element, driven by electroosmotic flow (EOF), superimposed on top of a steady, pressure driven throughput flow. Flow in the crossed arms of the oscillatory mixing element is driven sinusoidally, and in a manner 90 degrees out of phase with each other. Numerical analysis of the oscillatory cross channel flow shows that chaotic mixing is generated by a periodic combination of stretching (which occurs via shear in the channels), and rotation (which occurs by means of the timing of the oscillations), making the system an effective tendril-whorl (TW) type flow. The size and characteristics of the chaotic region and the downstream dispersion patterns are a function of a Strouhal number and the ratio of the throughput and oscillatory flow velocities. Evidence of chaotic mixing in the system is presented based on the analysis of experimental data, and comparison with the predictions of numerical computations.

Wednesday 4:20 Room 104/105

RM14

**The potential for micron scale spatially resolved rheology using classical nano-indentation techniques**

Chris C. White<sup>1</sup>, Peter Drzal<sup>1</sup>, and Mark Vanlandingham<sup>2</sup>

<sup>1</sup>*Building and Fire Research Laboratory, NIST, Gaithersburg, MD 20899;* <sup>2</sup>*Weapons & Materials Research Directorate, U. S. Army Research Laboratory, Aberdeen Proving Gro, MD 21005*

Nanoindentation has been proposed as a method to generate microscale spatially resolved rheological and adhesion measurements of soft materials. This is a new application of a well-established technique in harder materials such as ceramics and metals. The theoretical foundation and historical development of the working equations for nanoindentation and traditional rheological instrumentation will be presented and discussed. The major difference between nanoindentation and the more classical rheological instrumentation is in the treatment of the instrument-

sample interface. To illustrate how the treatment of the instrument-sample interface affects the data a series of measurements was performed on a cured epoxy, poly(methyl methacrylate), (PMMA), and two different crosslink density poly(dimethyl siloxane) (PDMS) samples. These samples are used to compare nanoindentation with classical rheological instrumentation measurements on polymeric samples in the glassy and rubbery plateau regions. Excellent agreement between bulk rheological data and dynamic nanoindentation data was observed for the two glassy materials and the less compliant of the two PDMS samples. More divergent results were observed for most compliant PDMS sample.

Wednesday 4:45 Room 104/105

RM15

**Measurements of viscoelastic functions in both time and frequency domains using nanoindentation**

Hongbing Lu, Gang Huang, and Bo Wang

*Mechanical and Aerospace Engineering, Oklahoma State University, Stillwater, OK 74078*

Methods are presented to measure viscoelastic functions defined in linear regime in both time domain and frequency domain. In time domain, we present methods to measure the creep functions through direct differentiation methods using load/displacement data and material parameter extraction methods by fitting load-displacement relation under condition that the Poisson's ratio is assumed constant. We also present a method to measure two independent viscoelastic functions for an isotropic material using nanoindentation. Finding two independent material functions through nanoindentation is necessary for polymers with glass transition temperature near test temperature, and for new materials with unknown Poisson's ratio. In frequency domain, we present a method to measure complex viscoelastic function under cyclic loading condition. Three polymers are used in validation, they are: polymethyl Methacrylate, polycarbonate and polyurethane. Nanoindentation results on viscoelastic functions are compared with results from uniaxial tests or dynamic mechanical analysis (DMA) tests to validate the nanoindentation techniques. The methods are then used in characterizing mechanical behavior of some biomaterials and (CNT, nanoclay) nanocomposites. The methods presented are appropriate for small amounts of viscoelastic materials such as nanocomposites, polymeric films/coatings and biomaterials in linearized viscoelastic regime.

Wednesday 5:10 Room 104/105

RM16

**A self-aligned apparatus for studying microscale flows**

Donggang Yao<sup>1</sup>, Zhe Xie<sup>2</sup>, and Qian Zou<sup>2</sup>

<sup>1</sup>*School of Polymer, Textile & Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332;*

<sup>2</sup>*Department of Mechanical Engineering, Oakland University, Rochester, MI 48309*

With the increasing interest in pressure-driven liquid flows in confined geometries, there emerges a need for the development of suitable devices for micro-rheological studies. The standard rheometry with macrogaps, however, has inherent disadvantages in adapting itself into a microscale version. On the other hand, compliance-based apparatuses are inappropriate for high-shear flows because of their extremely low load capacity and small allowable strain and strain rate. In this paper, a self-aligned device that involves a pair of parallel disks with the bottom one fixed and the top one floated is presented. A point load is applied at the center of the floating plate, for adjusting the gap size and centering the top plate. The applied load is balanced by the upward force inside the liquid disk resulting from viscous flow. Due to the complete axisymmetry in terms of the geometry and the stress field, the top plate will be self-aligned in reference to the bottom plate. The self alignment mechanism and the design principle of the device were verified using experiments with water as the testing liquid.

## Symposium SC Suspensions and Colloids

Organizers: Jan Vermant and Dan Klingenberg

Wednesday 1:50 Room 107

SC23

### **Hybrid simulations of the rheology of colloidal dispersions in simple and polymeric fluids**

Victor Pryamitsyn and Venkat Ganesan

*Chemical Engineering, University of Texas at Austin, Austin, TX 78746*

Many practically important complex fluid systems, such as colloidal particles dispersed in solvent media, surfactant mixtures etc. are multicomponent in nature. In such situations, to simulate dynamical and flow situations requires one to account for the hydrodynamical response of the solvent(s) along with the dynamics of the primary constituent. In this talk we present the methodology and the results of a two-level simulation approach combining conventional molecular dynamics ideas with dissipative particle dynamics (DPD) approach to address the dynamical properties of solutes in complex fluid solvents. In this approach, the solvent particles are represented as soft particles interacting through both conservative and dissipative forces. In contrast, the solute particles are represented as Lennard Jones particles of the appropriate size. To incorporate the hydrodynamic interactions between the solute and the solvent, the conventional DPD forces are phenomenologically modified to include additional rotational degrees of freedom transmitting shear forces from the solvent to the colloid. We first present "proof-of-principle" demonstration that our method reproduces the correct dynamical and rheological properties of colloidal suspensions in simple fluid solvents (including hydrodynamic interactions). Our results focus on the equilibrium and shear induced self-diffusivity and the steady state viscosity of the suspension. Subsequently, we present results pertaining to the equilibrium diffusivity and shear rheology of particles in polymeric solutions and melts. We focus on the influence of macromolecular relaxation processes on the suspension transport properties as well as the effect attractive interactions between polymers and particles have upon these properties.

Wednesday 2:15 Room 107

SC24

### **Study of a dissipative particle dynamics based approach for modeling suspensions**

Nicos S. Martys

*National Institute of Standards and Technology, Gaithersburg, MD*

A dissipative particle dynamics (DPD) based approach for modeling suspensions is examined. A series of tests are applied comparing simulation results to well established theoretical predictions. The model recovers the dilute limit intrinsic viscosity of Einstein and provides reasonable estimates of the Huggins coefficient for semidilute suspensions. At higher volume fractions, it was necessary to explicitly include lubrication forces into the algorithm as the usual DPD interactions are too weak to prevent overlaps of the rigid bodies and account for other related effects due to lubrication forces. Results are compared to previous studies of dense hard sphere suspensions using the Stokesian dynamics method and experimental data. Comparison of relative viscosity values determined from strain controlled shearing versus stress controlled shearing simulations are also given. The flow of spheroidal objects is studied. The rotation of a single spheroid under shear is consistent with the predictions of Jeffery. Simulations of sheared spheroids at higher volume fractions produce an ordered phase.

Wednesday 2:40 Room 107

SC25

### **Diffusion and reaction of Brownian particles in a dense suspension of traps**

Mark W. Vaughn

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409*

Much progress has been made in modeling reactive Brownian particles diffusing in and reacting with a suspension of stationary traps. An effective and efficient method to describe such a reacting system is based on first-passage time distributions, from which the particle survival time distribution can be obtained. The effective reaction rate coefficient of the suspension can be determined from the survival time. This method is particularly effective for fast reactions and for complex, dense suspensions. The analysis presented here addresses systems in which the reacting species can undergo diffusion and reaction in the continuous phase, as well as absorption and finite reaction at the trap surface. The diffusion path is divided into a series of first-passage regions and the probability of the particle

being consumed in each of these regions is considered. Similarly, when a particle approaches a trap, the probability of trapping is determined from the flux boundary condition. The method is effectively a probabilistic solution of the reaction-diffusion equation. The effect of suspension structure and surface reaction rate is discussed, as well as the relationship between the survival time of a particle and the permeability of the suspension.

Wednesday 3:05 Room 107

SC26

### **The elastic and plastic properties of disordered soft particle pastes**

Jyoti Seth<sup>1</sup>, Michel Cloitre<sup>2</sup>, and Roger T. Bonnecaze<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712;* <sup>2</sup>*Laboratoire Matiere Molle et Chimie, ESPCI, Paris, France*

Many concentrated materials consist of soft particles (polymer micelles, dendrimers, grains of nematic crystals, microgels, emulsions, and elastic and polymer coated particles) packed and deformed into an amorphous state. These pastes and their rheology are important, for example, in ceramic processing and dense surface coatings of submicron particulates. Previous investigations have shown that the rheological behavior of soft particle pastes is universal, and a key parameter to correlate and compare the data is each paste's elastic shear modulus. Recent modeling, though, has shown the osmotic pressure of the paste is in fact the key parameter. Apparently, the shear modulus is a convenient surrogate for the osmotic pressure.

We present theoretical simulations showing that in fact the osmotic pressure and shear modulus are approximately equal for most highly concentrated, amorphous suspensions of elastic particles. Three dimensional, periodically replicated, amorphous packings of monodisperse, elastic spheres are generated for a range of concentrations above maximum packing for hard spheres. Touching spheres are assumed to be in Hertzian contact, and the compressed suspension is relaxed to an equilibrium initial state. The shear and normal stresses, shear modulus and the osmotic pressure are then determined as a function of the affine shear strain and concentration. The shear modulus is found to be approximately equal to the osmotic pressure except at the highest concentrations. The yield point of the material is also determined by finding the strain at which the affinely sheared material no longer relaxes to its initial configuration. From this yield point we also determine the yield stress for the continuously deformed paste. The theoretical shear moduli, yield points and yield stresses as a function of concentration and sphere mechanical properties are shown to compare well with experimental observations. A scaling analysis is presented to explain their dependency on concentration.

Wednesday 3:55 Room 107

SC27

### **Understanding particle-surface interactions in colloidal gels from wall-slip**

Angelica M. Sanchez and Saad A. Khan

*Chemical engineering, North Carolina State University, Raleigh, NC 27695*

Wall slip phenomenon in colloidal gels and its relationship to the interactions between gel particles and the surface of the rheometer plates are examined. Gels composed of fumed silica nanoparticles (particle size  $\sim 12$  nm, surface area  $\sim 200$  m<sup>2</sup>/g) dispersed in non-polar and polar organic solvents are used. The surface of the silica particles is modified with several alkyl chain lengths and different surface coverage (up to 70% of the silanol groups reacted). Two types of parallel-plate surfaces are employed: hydrophobic (low surface energy) and hydrophilic (high surface energy). Dynamic shear experiments (time and stress sweeps) are performed using hydrophobic and hydrophilic plates as well as 'standard' stainless steel and serrated plates. The last two geometries are employed as a reference for the slip 'maximum' and 'minimum' limits, respectively. The onset of slip is monitored via two independent techniques: non-linearity of the wave shape and flow visualization. In addition, the slip velocity is calculated and correlated to the specific particle and plate surface chemistries. Our experiments show that the flow visualization method allows not only to observe the occurrence of wall slip but also to quantify the velocity at which the layer of fluid adjacent to the wall moves as the sample starts to slip, i.e., the CCD camera captures the start of the slip process at the instant the strain wave deviates from its sinusoidal shape. Gels containing hydrophobic fumed silica particles seem to be less susceptible to slippage when the surfaces of the rheometer plates possess a lower surface energy (hydrophobic surface). On the other hand, gels containing hydrophilic fumed silica particles start to slip at lower stress values than with the standard stainless steel plates. These results are explained in terms of specific interactions between the particles in the colloidal gel and the rheometer surface plates.

Wednesday 4:20 Room 107

SC28

**Complex rheology and modeling of a thixotropic suspension**Anne M. Grillet<sup>1</sup>, Rekha R. Rao<sup>1</sup>, Lisa A. Mondy<sup>1</sup>, Stacie Kawaguchi<sup>2</sup>, and Douglas B. Adolf<sup>3</sup><sup>1</sup>*Multiphase Transport Processes, Sandia National Laboratories, Albuquerque, NM 87185-0834;* <sup>2</sup>*Sandia National Laboratories, Albuquerque, NM 87185;* <sup>3</sup>*Materials and Process Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185*

Rheology of a model suspension of alumina particles will be presented that demonstrates the complex response of this thixotropic material. In order to simulate the experimental data, a bond structure model that relates particle bridging to the viscosity has been developed. In the limit of an infinitely fast response, this model simplifies to the Carreau-Yasuda model which predicts a shear thinning viscosity, but assumes the viscosity responds instantaneously to changes in the shear rate. The first order micro-structural model incorporates an additional scalar evolution equation for the extent of reaction and does an impressive job of capturing the critical suspension behavior, including the time dependence and hysteresis seen in viscometric flow. Unfortunately, these suspensions show additional complexity in their rheological response that was not captured by these models.

For most thixotropic suspensions, the time required to form structure is longer than the time constant to break it down. For this suspension, the time constant at a given shear rate was also dependent on the previous rate. If the previous shear rate was high, the time required to reach equilibrium was longer than if the previous shear rate was lower. This behavior was not captured by a simple initial structure dependence in the previous models. Thus, we have added an additional dependence on the initial bond structure and the prediction of the transient rheology was substantially improved while maintaining excellent agreement with the steady shear viscosity.

We have begun incorporating these models into a finite element code developed at Sandia that will allow us to simulate more complex free surface flows. Results for the first order bond structure model in fiber extrusion will be presented.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Wednesday 4:45 Room 107

SC29

**Thixotropy and rheopexy of aggregated dispersions with wetting polymer**Andrei Potanin*Imation Corp., Oakdale, MN 55125*

Different types of thixotropy of aggregated dispersions of magnetic metal, non-magnetic iron oxide and carbon black particles in organic solvents with a polymer containing pendant wetting groups are studied. Thixotropic behavior depends on the type of aggregation which determines the type of structural recovery in and after shear. Metal particles form denser aggregates combined into flocs or networks recoverable in or after shear, which results in positive thixotropy with up-shear stress-vs.-shear-rate curves running above down-shear curves. By contrast, iron oxide and carbon black particles form looser aggregates which re-flocculate slower in shear and do not re-flocculate at all at rest after shear, which results in rheopexy with recovery strongly accelerated by shear and negatively thixotropic loops. Viscoelastic moduli of the latter systems are determined by their shear history, e.g.,  $G'$  decreases with the preceding shear rate and doesn't recover. The effect of the wetting polymer on time-dependant phenomena is twofold: it suppresses thixotropy by consolidating aggregates, but slows down recovery, so that rheopexy is maximized at certain polymer-to-pigment ratios. Furthermore, two types of rheopexy are discriminated. Recovery rate of carbon black dispersions is controlled by the current shear rate only, resulting in thixotropic loops strongly dependent on sweep time. On the other hand, recovery rate of iron oxide dispersions has a long memory of shear history, which leads to thixotropic loops almost insensitive to sweep time. The difference is attributed to slow shear-induced dilation/shrinkage of aggregates built from elongated iron oxide particles, as opposed to stable aggregates of carbon black.

Wednesday 5:10 Room 107

SC30

**Thixotropy by magnetic resonance imaging (MRI)**Philippe Coussot<sup>1</sup>, Francois Bertrand<sup>1</sup>, Hieu-Thao Huynh<sup>1</sup>, Sebastien Jarny<sup>1</sup>, Nicolas Roussel<sup>2</sup>, and Stéphane Rodts<sup>1</sup><sup>1</sup>Institut Navier, LMSGC, Champs 77420, France; <sup>2</sup>LMSGC, Champs, France

Thixotropy may induce strong time-dependent flow heterogeneities in suspensions or pastes, which may preclude obtaining relevant information concerning the material behavior from conventional (macroscopic) rheometry. When these heterogeneities occur within a geometry in which the exact stress distribution is well controlled, these effects provide local information from which the effective rheological behavior of the material may be deduced. The recent improvement of MRI techniques makes it possible to determine the velocity profile within a suspension over a time shorter than 10s. We carried out experiments with three typical thixotropic systems exhibiting a characteristic time of thixotropy much larger than 10s: a laponite suspension, a bentonite suspension (Raynaud et al., *J. Rheol.*, 46, 709 (2002)) and a white cement paste. For all materials we first observed a viscosity bifurcation effect: the local shear rate tends either to zero or to a value larger than a finite value (Coussot et al., *Phys. Rev. Lett.*, 88, 218301 (2002)). Then we measured the velocity profiles in time during typical thixotropy experiments: start up flow after different times of rest and abrupt change of the rotation velocity of the inner cylinder. In particular these data show that the start up flow results from the progressive erosion of the initially unsheared region, and that the steady state depends on the flow history (or more precisely here the time of rest). A further rheological interpretation of these results requires to use a thixotropy model. We propose a complete comparison of our data with the predictions of a simple model of this type (Roussel et al., *J. Non-Newton. Fluid Mech.*, 117, 85 (2004)).

## Symposium SA Self-Assembled & Associating Fluids

Organizers: Srinivasa R. Raghavan and Yenny Christanti

Wednesday 1:50 Room 108/109

SA10

**Linear and non-linear rheology of mixed anionic surfactant solutions**Paloma Pimenta<sup>1</sup> and Eugene Pashkovski<sup>2</sup><sup>1</sup>Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08854; <sup>2</sup>Colgate Palmolive Company, Piscataway, NJ 08855

The linear and non-linear rheology of mixed anionic viscoelastic solutions was studied using strain and stress controlled experiments. First, dynamic oscillation experiments were performed and the linear viscoelastic parameters, i.e. the elastic plateau modulus and the relaxation time were measured. This linear rheology data was analyzed in terms of the Maxwell model, which allowed for the calculation of the reptation time and breaking time of the micelles ( $\tau_{rep}$  and  $\tau_b$ , respectively). Results show that, surprisingly, the value of the plateau modulus,  $G_0$  significantly increases with salt concentration,  $c_s$ , while  $\tau_b$  decreases by one order of magnitude. The strong effect of  $c_s$  on the material parameters and microstructure of rod-like micelles allowed for systematic investigation of the effect of these parameters on the non-linear flow. For samples with relatively long  $\tau_b$ , the quasi-static flow diagram shows a stress peak, followed by a metastable branch, whereas for samples with relatively short  $\tau_b$ , this phenomenon is never observed. Transient flow experiments further reveal the significance of the microscopic dynamic parameters. Shear stress time series recorded at constant shear rates show a strong dependence of the stress fluctuations on the material parameters. Above the critical shear rate,  $\dot{\gamma}_{c2}$ , the amplitude of stress fluctuations,  $\Delta$ , was found to scale as  $\Delta = G_0 [\tau_b (\dot{\gamma} - \dot{\gamma}_{c2})]^\beta$ , where  $\beta \sim 0.5$ ;  $G_0$  is the plateau modulus and  $\tau_b$  is the breaking time.

Wednesday 2:15 Room 108/109

SA11

**Effect of a block copolymer on the contour length and rheology of a solution of wormlike micelles of a zwitterionic surfactant**Arup Nandi<sup>1</sup>, Eric W. Kaler<sup>1</sup>, Phillip Sullivan<sup>2</sup>, and Yiyan Chen<sup>2</sup><sup>1</sup>*CMET, Department of Chemical Engineering, University of Delaware, Newark, DE 19716;*<sup>2</sup>*Schlumberger, Sugar Land, TX 77478*

Alkyl-betaines are zwitterionic surfactants which are known to form wormlike micelles in aqueous media. The solutions are viscoelastic. Unlike charged wormlike micelles (made from ionic surfactants), the rheology and microstructure of zwitterionic surfactants cannot be tuned by the addition of salt. Here, we report on how a [C12]([EO]32)[C12] block copolymer can be used as an additive to tune the micellar contour lengths of wormlike micelles. The micelles are made of an alkyl-betaine (having a C22 chain) surfactant. The microstructural evolution was studied using classical rheology and the persistence length was determined using rheo-optics. Addition of the block copolymer reduced the contour length of the micelles while the other length scales (persistence length, network mesh size and the entanglement length) were unaltered. This suggests that the large hydrophilic head group of the block copolymer cuts the micelles by favoring the formation of end caps. The contour length when plotted against the relaxation time of the network shows a dependence that closely follows the reptation model proposed by deGennes. The hypothesis that the block copolymer acts as a micellar "scissor" is confirmed by dynamic light scattering.

Wednesday 2:40 Room 108/109

SA12

**Scaling theory at gelation point: chitosan concentration and temperature effects**Jaepyoung Cho<sup>1</sup>, Marie-Claude D. Heuzey<sup>1</sup>, Andre Begin<sup>2</sup>, and Pierre J. Carreau<sup>1</sup><sup>1</sup>*Chemical Engineering, Ecole Polytechnique, Montreal, Quebec H3C 3A7, Canada;* <sup>2</sup>*Food Research and Development Center, Saint-Hyacinthe, Quebec J2S 8E3, Canada*

Heat-induced isothermal gelation tests were performed for acidic aqueous solutions of chitosan ( $M_w = 850,000$  g/mol ( $PI = 2.8$ ) and degree of deacetylation = 93%). The dynamic rheological properties throughout the physical gelation were measured as functions of chitosan concentration and temperature. The oscillatory shear data obtained was used to verify the scaling law [Chambon and Winter, JOR, 1987] at the gelation point. At the gelation point ( $G' \sim G'' \sim \omega^n$ ), the exponent  $n$  is dependent on chitosan concentration ( $n = 0.79$  for 1.72 wt% and 0.57 for 2.58 wt%), but not on temperature. The gelation time decreases with increasing temperature and concentration. The zero shear viscosity ( $\eta_0$ ) and longest relaxation time ( $\tau_{max}$ ) determined from the Carreau-Yasuda model, and the equilibrium modulus  $G_e$  were analyzed in terms of the relative distance of gelation time ( $\epsilon$ ) at each condition, in relation with the dynamic scaling theory for the viscoelasticity of cross-linking polymers near the gel point [Martin et al., Phys. Rev Lett, 1988]. The three properties shows a power-law relationship with ( $\epsilon$ ):  $\eta_0 \sim \epsilon^{-k}$ ,  $\tau_{max} \sim \epsilon^{-y}$  and  $G_e \sim \epsilon^z$ . The three index increase with temperature (between 30 and 45oC), with  $k$  going from 0.61 to 2.3,  $y$  from 1.6 to 6.7 and  $z$  from 1.1 to 2.2 for the 2.58 wt% chitosan concentration. The  $k$ ,  $y$  and  $z$  values increase with increasing chitosan concentration in isothermal conditions. The dynamic scaling theory used for chemical gels has been also applied to physical gels. This theory predicts a relationship between the three indexes, i.e.  $y = z + k$ . This relationship is verified for our system only at low temperatures (up to 40oC).

Wednesday 3:05 Room 108/109

SA13

**Evaluation of nanoparticle arrays templated by self-assembled block copolymer gels**

Danilo C. Pozzo and Lynn M. Walker

*Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213*

Three-dimensional spatial organization of inorganic nanoparticles or nanometer-sized biomolecules is particularly important in emerging nanotechnology applications involving optical materials, controlled-release of proteins and separation of biomolecules in gel electrophoresis. Nanoparticle templating through the self-assembly of amphiphilic block copolymers in selective solvents presents an elegant bottom-up approach to achieving this goal. However, there is a lack of systematic experimental studies that characterize the influence of organic and inorganic fillers on the three dimensional organized copolymer gels. We are utilizing water-soluble triblock copolymers (PEO-PPO-PEO) to provide thermoreversible micellar-cubic templates with typical dimensions of tens of nanometers. The temperature-dependent amphiphilic nature of the copolymers provides control of the structure and allows the use of

pre-made silica and gold nanoparticles as well as globular proteins. Using rheology and small-angle neutron scattering (SANS), we characterize the influence of nanoparticle loading on both the macroscopic sample properties and on the local structure of the gel. By using solvents containing isotope mixtures in SANS we are able to separately study the structure of the organic and inorganic phases through the variation of the neutron scattering contrast. Using contrast matching techniques, we demonstrate that the template approach is feasible as reasonable quantities of nanoparticles are incorporated into the block copolymer gel without destroying the ordered structure. It is also found that the nanoparticles are templated by the polymer gel and that the level of organization is dependent on a number of variables. We quantify the results by studying the influence of relative concentration, relative dimensions and temperature on both the nanoscale structure and macroscopic composite properties.

Wednesday 3:55 Room 108/109

SA14

### **Multiple gelation mechanisms in block copolymers**

Prashant Mandare<sup>1</sup> and H. Henning Winter<sup>2</sup>

<sup>1</sup>*Chemical Engineering, University of Massachusetts Amherst, Amherst, MA 01003;* <sup>2</sup>*Chemical Engineering and Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003*

Rheological experiments of gelation and reverse gelation will be discussed for a model polymer (nanophase separated block copolymers with spherical domains) that is able to gel in several different ways: by network formation, by crystallization, or by glass transition. Here, gelation is viewed as the growth of sample-spanning connectivity in a soft material, with all its consequences. Rheologically, gelation induces a transition from liquid to solid. This is easy to achieve experimentally but difficult to explain in a fundamental way. Most puzzling is the observation of the universal rheological behavior at the instant of transition (gel point). Linear viscoelasticity at the gel point is independent of the specific connectivity mechanism (attraction or repulsion) or whether the material is in equilibrium or out of equilibrium (soft glass). Material differences only affect the rheological parameters ( $S_c$ ,  $n_c$ ,  $l_0$ ,  $l_{max}$ ). Physical gels distinguish themselves with a longest relaxation time  $l_{max}$  that is finite due to the finite life time of the respective connectivity mechanism(s).

Wednesday 4:20 Room 108/109

SA15

### **Experimental characterization of critical gel behavior of thermoplastic poly(esterurethanes)**

Dario Nichetti<sup>1</sup> and Nino Grizzuti<sup>2</sup>

<sup>1</sup>*R&D, Chiorino Lab, Biella 13900, Italy;* <sup>2</sup>*Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli "Federico II", Napoli 80125, Italy*

This work describes an experimental study of the phase transition behaviour of a series of linear thermoplastic poly(esterurethane) as a function of molecular weight and hard-soft block ratio. In fact, TPUs are randomly coupled multi-block copolymers of alternating soft and hard segments and their thermodynamic immiscibility at low temperature results in a phase-separated, micro-domain structure. Upon cooling from the melt, both microphase separation and crystallization of the hard phase can be observed, leading to the formation of ordered domains. The morphology of the phase-separated system is responsible of the final properties of TPUs. Phase transition, however, can be also relevant during the processing stages, as it considerably affects the rheological response of the material.

Measurements of viscoelastic moduli in oscillatory flow demonstrate that the phase transition can be rationalized in terms of a sol-gel transition. In particular, the critical gel point under solidification conditions can be determined a frequency-independency loss tangent at low frequencies. The effect of both molecular weight and chemical structure on these features has been investigated. In particular, the results show that the critical gel parameters,  $S$  and  $n$ , obtained by cooling the melt are linearly related.

Wednesday 4:45 Room 108/109

SA16

**Extrusion of triblock and pentablock copolymer blends**

Alhad Phatak, Vincent C. Holmberg, Christopher W. Macosko, and Frank S. Bates

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

We report studies on the extrusion of blends of nearly monodisperse triblock and pentablock copolymers composed of poly(cyclohexylethylene) (C) and poly(ethylene) (E). Recently (Phatak et. al., J. Rheol, in press), we found that extrudates of lamellae-forming CEC triblock and CECEC pentablock copolymers displayed contrasting lamellar alignment behavior and dramatically different surface characteristics. Lamellae in CEC extrudates flipped from a mixed to a perpendicular alignment with increasing extrusion rate, while CECEC lamellae were oriented in the perpendicular alignment under all processing conditions. At comparable shear stresses above a critical value, the CEC extrudate surfaces had relatively low amplitude (1-3  $\mu\text{m}$ ) random roughness while the CECEC extrudates had a textured surface, with periodic  $\sim 50$   $\mu\text{m}$  undulations that resemble a sharkskin morphology. These differences are attributed to the rheological consequences of the center bridging C block in the pentablock copolymer. In order to further probe the effect of chain architecture by continuously varying the degree of lamellar bridging, blends of the CEC and CECEC polymers were prepared. CEC/CECEC blends were extruded through a slit die at various processing speeds below the order disorder transition temperatures. Small angle x-ray scattering was used to characterize bulk lamellar orientation and extrudate surface features were studied using a combination of optical microscopy and profilometry measurements. Addition of only 20% CEC nearly eliminates the severity and periodicity of surface roughness associated with pure CECEC samples. This counter-intuitive result clearly establishes the dichotomy between bulk properties and surface fracture effects induced by fast processing flows, and emphasizes the role of chain architecture in block copolymer processing. We expect extensional rheological measurements to shed light on the mechanisms governing this phenomenon.

Wednesday 5:10 Room 108/109

SA17

**Relationship between phase behavior and actuation in smectic elastomers**Ingrid A. Rousseau<sup>1</sup> and Patrick T. Mather<sup>2</sup><sup>1</sup>*Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269;*<sup>2</sup>*Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106*

Significant attention has been given to the reversible actuation and so-called soft elasticity of nematic liquid crystalline elastomers, particularly from the group of H. Finkelmann. In these systems, samples prepared as uniaxial monodomains are observed to spontaneously expand on cooling from the isotropic to nematic states. Conversely, when the samples are heated to induce isotropization, shrinkage along the same direction is observed. Given the large strains and low modulus, such materials have been suggested to serve as artificial muscles stimulated either by heating and cooling or even by light. Our group has focused on the preparation and characterization of siloxane-based smectic analogs with the hypothesis that the higher level of ordering presented by smectics would significantly alter the nature of soft actuation. We have thus prepared a series of smectic elastomers (of varying composition) and linear polymeric analogs, characterizing their phase behavior by thermal analysis, x-ray scattering, and light microscopy. We have found that the materials generally adopt a smectic-C phase with compositionally adjustable clearing transition. Furthermore, the materials feature fractional vitrification at temperatures near but lower than the clearing transition. Solid rheological properties in shear as well as shape memory behavior in tension were investigated, revealing a clear relationship between the observed phase behavior and macroscopic linear and nonlinear mechanical response. Our presentation will focus on the intimate connection between the underlying phase behavior and unique shape memory behavior of these new elastomers.

## Symposium MS Entangled Melts & Solutions

Organizers: Lynden A. Archer and Dimitris Vlassopoulos

Wednesday 1:50 Theater

MS19

### **Viscoelastic properties of cyclic polyethylene**

Jian Wang and Gregory B. McKenna

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

The linear viscoelastic properties of cyclic polyethylene (PE) with molecular weights ranging from 56,000 to 231,000 g/mol were studied[1]. Dynamic experiments show that the flow activation energy of the cyclic PE is higher than the value of linear PE. The obtained plateau modulus value is 2.03 MPa, which is also higher than that of linear PE. Steady flow experiments in a parallel plate configuration show that the zero-shear-rate viscosities of the cyclic PEs are higher than those of their linear counterparts by one to three orders of magnitude, and follow an exponential-like dependence on the sample's molecular weight. The results in this study are significantly different from the literature results for other cyclic polymers. It was found that the linear viscoelastic properties of the cyclic PE are similar to those that have been found on the long chain branched PE, which indicates that the relaxation of the rings is greatly suppressed by certain kinds of topological constraints; the interpenetration of the loops is considered the main cause of this.

[1] The Cyclic Polyethylenes were synthesized by R.H. Grubbs and his group at California Institute of Technology.

Wednesday 2:15 Theater

MS20

### **Motion of branch point in asymmetric star polymers**

Jung Hun Lee, Lewis J. Fetters, and Lynden A. Archer

*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853*

Relaxation dynamics in a series of 1,4-polyisoprene asymmetric star polymers are investigated experimentally and theoretically in order to identify the motion of the branch-point. The branch point has a quite entangled short arm ( $M_{\text{as}}/M_{\text{e}} = 7$ ) and two long arms with different molecular weights ( $M_{\text{al}}/M_{\text{e}} = 7 \sim 44$ ). The degree of asymmetry in the given architectures  $b = M_{\text{al}}/M_{\text{as}}$  varies from 2 to 6. At first, we observe the measured loss modulus more sensitively reflects a transition in the governing dynamics as the asymmetry increases. This finding suggests a possibility to describe the governing dynamic transition by constituent structural terms. Recently proposed microscopic model frame for asymmetric star polymers contains an adjustable parameter  $p$  to describe the motion of branched point. A simplest scaling approach from the terminal time scales provides a simple relationship between  $p^2$  and a given structure. The proposed model predictions provide quite acceptable agreements with the measured stress relaxations of asymmetric star polymers without any adjusting  $p^2$  values.

Wednesday 2:40 Theater

MS21

### **Role of branch point friction in the relaxation of H-polymers from detailed, 3is-long, atomistic molecular dynamics simulations**

Nikos Karayiannis and Vlasis Mavrantzas

*Institute of Chemical Engineering and High Temperature Chemi, FORTH, Patras, Greece*

Model H-shaped polyethylene (PE) melt systems containing up to 500 carbon atoms per chain have been subjected to detailed, 3is-long equilibrium NPT molecular dynamics (MD) simulations. Thoroughly equilibrated initial configurations for the MD studies have been obtained with the novel double-bridging Monte Carlo method [Karayiannis et al., Phys. Rev. Lett. (2002)]. The MD simulation results provide convincing evidence for the different relaxation mechanisms exhibited by an H-polymer melt: a fast relaxation due solely to arm breathing (on the order of a few ns, for an H\_300\_50 melt), and a slow branch point diffusion accompanied by a sluggishly slow backbone diffusivity due to reptation (on the order of a few is, for the H\_300\_50 melt). The MD simulation data have further: (a) demonstrated that the center-of-mass diffusivity in an H-polymer follows faithfully that of the branch points, thus validating from first-principles the assumption of the McLeish-Larson pom-pom theory that all

friction in an H-molecule is concentrated at the branch points, and (b) revealed a dramatic slow of the self-diffusion coefficient  $DG$  when the polymer molecular weight  $M$  exceeds approximately 2,400 g/mol.

Wednesday 3:05 Theater MS22  
**Linear-viscoelastic properties of long-chain branched polyolefin melts and their relation to molecular structure**

Helmut Münstedt, Dietmar W. Auhl, Florian Stadler, Jens Stange, and Claus Gabriel  
*Institute of Polymer Materials, University Erlangen-Nürnberg, Erlangen D-91058, Germany*

This paper presents a survey on the influence of long-chain branches on linear-viscoelastic properties of polyolefin melts. The rheological results are interpreted with respect to the molecular and entanglement structure using models available in literature. The materials chosen are linear and long-chain branched polyethylenes and polypropylenes. Among these are commercial products and especially polymerized or modified laboratory materials. The molecular characterization is accomplished by size exclusion chromatography coupled with light scattering. Creep experiments are performed in order to determine the zero-shear rate viscosity  $\eta_0$  and the recoverable compliance. For linear polyethylenes the relationship  $\eta_0 \sim M_w^{3.6}$  is found independent of polydispersity. This result is taken as the basic to assess the influence of long-chain branching on  $\eta_0$ . From  $\eta_0(M_w)$  of variously branched polyethylenes in comparison to linear samples conclusion with respect to the branching topology are drawn. By using the results found for polyethylenes the structure of long-chain branched polypropylenes generated by electron beam irradiation is analyzed. It is found that the topology and the length of the branches and following from that their interaction due to entanglements can be changed significantly according to the irradiation conditions. Blends from linear and long-chain branched polypropylenes are investigated in order to get some insight into the effect of the number of branched molecules with a defined structure on linear-viscoelastic properties.

Wednesday 3:55 Theater MS23  
**An examination of entangled star polymers under shear using birefringence**

Amy Tezel and Gary Leal  
*Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106*

Star polymers have a single branch point and thus understanding their dynamics is a useful first step in gaining understanding of the more complicated, multiply branched polymers that are commonly used in processing today. In the linear viscoelastic regime, the single branch point has already been demonstrated to have a significant effect on the relaxation time spectrum, differentiating the star polymer from its linear counterpart. As shear rates reach the order of the inverse of the longest relaxation time, it has been shown for linear polymers that convective constraint release becomes an important relaxation mechanism. Convective constraint release is also significant for star polymers as we have recently demonstrated in steady shear experiments, and it is expected that this will mitigate the differences between linear and star polymer once they are subjected to sufficiently high shear flows. Using two color flow birefringence which directly measures the birefringence and orientation angle, together with traditional rheological measurements, we will examine and compare the relaxation mechanisms that dominate and contribute to the behavior of the solutions of four arm stars and linear polymers with the same span molecular weight. Various flow conditions will be explored including startup of flow and step changes in shear rate, shear reversal, and steady shear.

Wednesday 4:20 Theater MS24  
**Nonlinear relaxation dynamics of entangled star polymers**

Lynden A. Archer and Jung Hun Lee  
*School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853*

We discuss the nonlinear flow properties of entangled star polymers in steady shear and step shear deformations. Model 3-arm polyisoprene stars with varying degrees of arm length asymmetry are used to investigate the effect of molecular architecture on nonlinear stress relaxation dynamics of entangled branched polymers. We find that as the molecular architecture is systematically varied from star-like (low asymmetry) to linear-like (high asymmetry), the flow curve manifest less shear thinning characteristics, and the step shear damping function becomes less strain softening. These observations are discussed in terms of mechanisms for convective acceleration of chain relaxation (CCR) and contour length deformation in branched molecules. Specifically, our results show that as the arm length

asymmetry is reduced, chain stretching and CCR become less important features of the nonlinear shear response of entangled stars. The effect of this observation on interfacial slip characteristics of star polymers (entangled and unentangled) is also discussed.

Wednesday 4:45 Theater

MS25

**Torque and normal force responses of branched polyethylene melts in reversing double-step strain flows**

Changping Sui and Gregory B. McKenna

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

Double-step strain histories, especially reversing flows, have provided severe tests of nonlinear constitutive equations for the viscoelastic response of narrow dispersed linear polymers in the past three decades. Recently, the reversing double-step strain histories have attracted interest for the testing of the nonlinear response of branched polymers. In the present study, single and three types (type B, C and D) of reversing double-step torsional experiments were performed on both commercial branched and linear polyethylenes (PEs); the torque and normal force responses were analyzed within the framework of the K-BKZ theory. Strain magnitudes as great as 8 were investigated. The comparison between the experimental data and the K-BKZ theory of the type B and C flows for the branched PEs and the comparison of type B flow for linear PE are in good agreement with previous studies, i.e. the K-BKZ theory provides a good quantitative description of the response of branched polymers in reversing flows while the opposite is the case for the linear polymers. In the type D flow, we found that the K-BKZ theory predicts both normal force and torque responses very well for branched Polyethylene. This was not so for the linear polyethylene. Consideration of the material damping functions will also be presented.

Wednesday 5:10 Theater

MS26

**The rheology and degradation of renewable resource polymers**

Patricia A. Daly and Graham M. Harrison

*Chemical Engineering, Clemson University, Clemson, SC 29642*

Polymers developed from renewable resources are increasingly becoming commercially viable. However, there are some limitations that must be addressed as they seek to compete with conventional, petroleum-based materials in large quantities. In particular, the mechanical properties are often inferior to traditional materials, and degradation at elevated (processing) temperatures is often rapid. In this work we investigate the rheological properties of copolymers and of blends of renewable resource polymers. In particular we focus on a series of PLA and PHA based blends that offer enhanced properties relative to the individual components. We find that the specific polymer architecture inherent in the polymers has a significant impact on the flow properties and on degradation. Both the dynamic rheology and transient degradation studies are presented for copolymers and polymer blends. The degradation kinetics are determined from the transient rheological results, and the impact of temperature and mechanical shearing is quantified.



# Thursday Morning

## Symposium FI Fluid Mechanics and Instability

Organizers: Radhakrishna Sureshkumar and Yong Lak Joo

Thursday 8:30 Room 104/105

FI1

### **Post-breakup asymptotics for a Giesekus jet**

Michael Renardy

*Mathematics, Virginia Tech, Blacksburg, VA 24061-0123*

We discuss the retraction of a filament of a Giesekus fluid following a surface tension driven breakup. A similarity solution describing the behavior near the breakup point is derived and given in closed form. The analysis differs significantly depending on whether a retardation time is included or not. Without retardation, the filament breaks over a finite distance at once, and the subsequent retraction is not consistent with slender body asymptotics.

Thursday 8:55 Room 104/105

FI2

### **Effect of flow instability on molecular conformation and drag**

R. Sureshkumar<sup>1</sup> and B. Sadanandan<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Washington University, Saint Louis, MO 63130;* <sup>2</sup>*Intel Corporation, Hillsboro, OR 97124*

Several experiments since the 1960s have shown that in viscoelastic creeping flows through porous and model porous media, the friction factor increases abruptly when the flow rate exceeds a critical value. This phenomenon has eluded explanation backed by analysis/simulations based on first principle models. Steady state flow simulations have not been able to robustly predict this phenomenon. It has been conjectured that the existence of elastic instabilities could result in drag-enhanced states. We have computed the nonlinear (finite amplitude) states that manifest after the onset of instability in viscoelastic flow through a periodic channel for Oldroyd-B and FENE-P models. These finite amplitude states have qualitatively different normal stress distributions as compared to those in the base flow. Small increase in the Weissenberg number (defined as the product of the fluid relaxation time and an inverse characteristic shear rate) from the critical point (predicted by linear stability analysis) can result in a large increase in the maximum normal stress. The feedback of this normal stress increase on the friction factor has been analyzed. It is shown that finite amplitude states resulting from viscoelastic flow instabilities in such geometries produce slightly higher drag compared to the base flow. This and the influence of molecular stiffness on the nonlinear states will be discussed.

Thursday 9:20 Room 104/105

FI3

### **Nonlinear hydrodynamics of time-dependent viscoelastic Taylor-Couette flows of dilute polymer solutions**

Dennis G. Thomas, R. Sureshkumar, and Bamin Khomami

*Chemical Engineering, Washington University, Saint Louis, MO 63130*

Prototypical flow geometries like cone-and-plate, parallel plate and Taylor-Couette flows have served as classical paradigms for theoretical investigation of hydrodynamic flow instability phenomena in viscoelastic flows under both isothermal and non-isothermal conditions. Linear stability theory and experiments have shown that these flows become unstable at a critical Weissenberg number and Reynolds number, and their post critical dynamics are generally three-dimensional and time-dependent. To date, the studies on post critical dynamics of this class of flows

have been very limited due to the fact that simulation of 3-D time-dependent viscoelastic flows is an extremely challenging task. Motivated by this fact, we have developed an Operator Splitting Influence Matrix Spectral (OSIMS) algorithm for computationally efficient simulation of 3-D time-dependent viscoelastic flows. The utility, accuracy and computational efficiency of OSIMS are demonstrated by examining the post critical dynamics of viscoelastic Taylor-Couette flow utilizing the Oldroyd-B constitutive equation which is a reasonably good model for the rheological description of dilute polymer solutions. It is known from linear stability theory that the viscoelastic Taylor-Couette flow is unstable to non-axisymmetric and time-dependent disturbances depending on the flow elasticity ( $E$ ), defined as the ratio of the Weissenberg number to the Reynolds number. It is also known that two types of secondary flow patterns emerge near the bifurcation point, i.e., ribbons or spirals. We have demonstrated via time-dependent simulations that the non-axisymmetric flow patterns corresponding to ribbons are more stable than spirals near and above the linear stability threshold for elasticity values between 0.03 and 0.15. Depending upon the magnitude of finite amplitude flow disturbances and flow strength, higher order nonlinear flow transitions can be expected to occur, and the spatial-temporal characteristics of these emerging nonlinear flow patterns are explored.

Thursday 10:10 Room 104/105

FI4

### **Dilute worm-like micellar solutions: Model and numerics in Taylor-Couette flow**

L. Pamela Cook and Louis F. Rossi

*University of Delaware, Newark, DE*

Through a microstructural bead-spring description a coupled stress/density model for the flow of dilute micellar solutions is presented. The model derivation systematically includes finite extent of the bead-spring, bead slippage, and finite extensibility of the springs. The slippage is a non-affine motion related to micellar break-up. The model reduces to the the Johnson-Segalman model with a non-monotone flow curve in the limit of no migration effects. Numerical calculations of the model in cylindrical Taylor-Couette flow are presented. The linear stability analysis of solutions along the flow curve demonstrates that inclusion of the higher-order stress terms in the model provides a selection mechanism in multi-valued regions of the underlying flow curve. The stress-strain curve exhibits a plateau as observed in experiments. Shear banding is predicted both in velocity gradients and in the alignment/ orientation of the bead-springs. Computed solutions are compared with laboratory experiments.

Thursday 10:35 Room 104/105

FI5

### **Slow flow hole pressure for a tube on one wall of a plane channel**

Bruce Caswell<sup>1</sup>, Vasileios Symeonidis<sup>2</sup>, and George E. Karniadakis<sup>2</sup>

<sup>1</sup>*Division of Engineering, Brown University, Providence, RI 02912;* <sup>2</sup>*Division of Applied Mathematics, Brown University, Providence, RI 02912*

The low shear-rate, limiting value of the hole pressure for a three-dimensional hole is shown to be determined by the solution of the Reiner-Rivlin problem, i.e. the inertialess flow of the Reiner-Rivlin fluid with constant coefficients. In plane flow the analogous problem is the pressure due to a slot transverse to the flow. This result was obtained by application of the Giesekus-Tanner (G-T) theorem to the Stokes flow field. Kearsley extended the Tanner-Pipkin analysis to a channel with a slot parallel to the flow. In this work it is shown that in three-dimensions the Reiner-Rivlin velocity field also satisfies the corresponding flow of an augmented second order fluid. As in G-T the pressure field for the higher order problem in the three-dimensional case is again given in terms of quantities calculated from the lower order problem. The Tanner-Pipkin hole pressure for the slot is that relative to the Newtonian value, assumed to be negligible. For the three-dimensional holes of this work the Tanner-Pipkin term is the hole pressure relative to the Reiner-Rivlin value which is not negligible. This is the theoretical motivation for our numerical study of the Reiner-Rivlin flow. The results to be presented employ a high order stiffly-stable scheme with spectral vanishing viscosity which has been adapted to handle flows of the Reiner-Rivlin fluid. The flow geometry is a plane channel (gap width  $H$ ) with a long tube hole (diameter  $d$ ) transversely mounted on one wall. Kearsley's analytical result for the parallel slot has been used to verify the numerical results for the Reiner-Rivlin fluid. The effect of inertia on the hole pressure for Newtonian fluids has also been calculated, and shown to be in good agreement with experimental results. For round holes the numerical results for the hole pressure differ from the Higatshitani-Pritchard formula as the hole size increases. The effect of both pressure driven (Poiseuille) flow and drag (Couette) flow in the channel flow on the hole pressure has also been investigated.

Thursday 11:00 Room 104/105

FI6

**A continuum mechanical gradient theory with application to turbulent flows**Mansour Alizadeh*Research, Aerospace, Tehran, Iran*

A gradient theory of grade two based on an axiomatic conception of a no local continuum theory for materials of grade  $n$  is presented. The total stress tensor of rank two in the equation of linear momentum contains two higher stress tensors of rank two and three. In the case of isotropic materials both the tensor of rank two and three are tensor-valued functions of the second order strain rate tensor and its first gradient so that the equation of motion is of order four. The necessary boundary conditions for real (dissipative) boundaries are generated by using so-called porosity tensors. This theory is applied to a velocity profile of a turbulent COUETTE flow of water. On the basis of these experimental data the material and porosity coefficients are identified by numerical algorithms like evolution strategies.

Thursday 11:25 Room 104/105

FI7

**Determination of the flow and mixing in a continuous mixer using 3D Finite Element****Methods simulation**Jozef L. Kokini and Bharani Ashokan*Department of Food Science, Rutgers University, New Brunswick, NJ 08854*

One of the major challenges in the food industry is the scale up and identification of alternative mixing geometries to achieve well mixed doughs. Mathematical modeling and computer simulation allow insights into the operation of mixing where physical measurements are not readily possible and validation experiments confirm the reliability of simulation results.

The objective of this work is to examine the flow and mixing in a 2" Readco Continuous Processor using a 3D FEM simulation. The simulation results have been validated with available experimental velocity data obtained using Laser Doppler Velocimetry (LDA). FEM simulations were performed with POLYFLOW (Fluent Inc.), which uses a mixed Galerkin formulation of the isothermal governing equations of motion and continuity.

Increasingly complex 3D geometries were developed to accurately represent the geometry and flow conditions in the continuous mixer and the predictions were compared with the velocities measured by LDA. Predictions by numerical simulation and observed experimental velocities in a plane perpendicular to the flow agree well at all representative points within the mixer. The predicted data for the velocity component in the direction of flow required careful definition of boundary conditions to obtain agreement with experimental data. The addition of paddles to the simulation geometry in the direction of flow improved the description of the boundary conditions by allowing the flow to develop sufficiently. The effect of periodic flow patterns on mixing behavior was also investigated with shear rate and mixing index analysis. Particle tracking analysis was conducted by allowing 1000 random particles to mix in the flow field. The analysis showed a greater probability of higher mixing indices as the residence time in the mixer increases.

The successful simulation of the continuous mixer geometry in 3D provides valuable insight into the mixing processes involved, and paves the way for efficient scale-up or redesign of mixers.

## Symposium SC Suspensions and Colloids

Organizers: Jan Vermant and Dan Klingenberg

Thursday 8:30 Room 107

SC31

### **NMR profilometry**

Stephen A. Altobelli<sup>1</sup>, Rekha R. Rao<sup>2</sup>, and Lisa A. Mondy<sup>2</sup>

<sup>1</sup>*New Mexico Resonance, Albuquerque, NM 87106*; <sup>2</sup>*Multiphase Transport Processes, Sandia National Laboratories, Albuquerque, NM 871850834*

We use NMRI (Nuclear Magnetic Resonance Imaging) to study the free surfaces of flowing neutrally buoyant concentrated suspensions. As Zarraga, Hill and Leighton (*J Rheol* **44**(2) 185 (2000)) pointed out, the free surface profile is related to normal-stress differences. Examples of rod dipping observed in concentrated suspensions flowing in a concentric cylinder vertical Couette device will be presented.

By using NMRI profilometry one may also observe de-mixing phenomena such as shear induced particle migration. We have seen particle concentration non-uniformities evolve in two ways. First, in suspensions of relatively large particles the particle concentration evolves radially, while in suspensions of fine particles a small vertical stratification has been observed.

It is also possible to observe free surfaces of arbitrary connectedness and complexity which might be difficult to observe by other techniques. Examples of complex free surfaces visualized in eccentric vertical Couette flows of viscous liquids and concentrated suspensions will be presented.

Thursday 8:55 Room 107

SC32

### **Properties of a concentrated suspension flowing through an abrupt expansion measured by NMRI**

Tracey Moraczewski and Nina C. Shapley

*Department of Chemical Engineering, Columbia University, New York, NY 10027*

Our research focuses on the behavior of dispersed particles in complex flows. One example is the flow of a concentrated suspension into an abrupt expansion, which can be encountered in such applications as materials processing or flow in the circulatory system. Fundamental understanding of such a system is limited, mainly due to the small amount of available experimental data and modeling calculations concerning suspensions in complex flow geometries. In this study, suspensions of neutrally buoyant, noncolloidal spheres in Newtonian liquids undergo steady, pressure-driven flow in abrupt, axisymmetric 1:2 and 1:4 expansions. Particle concentration and velocity profiles are obtained by nuclear magnetic resonance imaging (NMRI). We aim to determine the particle properties and flow conditions (e.g. particle volume fraction, particle and flow Reynolds number, particle-tube radius ratio, expansion ratio) that lead to the accumulation or depletion of particles in recirculating flow regions such as the corner vortices. Both accumulation and depletion have been observed, depending on experimental conditions, in a few previous studies of suspension flows in various complex geometries. Recent results from expansion flow experiments will be presented.

Thursday 9:20 Room 107

SC33

### **Frame invariant suspension rheology applied to the abrupt contraction and expansion**

Ryan M. Miller<sup>1</sup> and Jeffrey F. Morris<sup>2</sup>

<sup>1</sup>*School of Chemical and Biomolecular Engineering, Georgia Tech, Atlanta, GA 30332-0100*; <sup>2</sup>*Energy Services Group, Research, Halliburton, Houston, TX 77032*

A frame invariant suspension rheology model is proposed. The rheological constitutive law is applied to the flow of a suspension through conduits of abruptly varying cross-section, specifically sharp-edged contractions and expansions in channel and axisymmetric tube flows. The methodology allows incorporation of the variation in flow type upon the rheology, and hence upon the stress-induced migration of suspended particles. Variation of flow type is extreme in the flows studied here, as the flow goes from simple shear upstream to nearly pure extension in the

throat of the contraction, and is vorticity dominated in the corner vortex. The role of flow type is captured through a frame-invariant measure we term the kinematic ratio, which is similar to measures proposed to describe, for example, strain rate thickening in polymer solutions. The kinematic ratio is a local measure given by a frame invariant rotation rate divided by the magnitude of the rate of strain. The frame invariant rotation rate is not given by the local vorticity (which is a frame dependent quantity) but instead is the material rotation rate relative to the local eigenvectors of the strain rate. A convenient means of modeling the stress is presented in terms of the local coordinates given by the strain rate eigenvectors, and the general framework is illustrated by several constitutive assumptions. We focus on the normal stress modeling and its influence: on streamlines; on the rate of particle migration leading, for example, to accumulation in the corners just upstream of a contraction; and on the ultimate steady particle distribution.

Thursday 10:10 Room 107

SC34

### **Diffusive coarsening of foams: von Neumann's law in 3D**

Andrew M. Kraynik<sup>1</sup>, Sascha Hilgenfeldt<sup>2</sup>, and Denis Weaire<sup>3</sup>

<sup>1</sup>Department 9114, Sandia National Laboratories, Albuquerque, NM 87185-0834; <sup>2</sup>Department of Engineering Sciences and Applied Mathematics, Northwestern University, Evanston, IL 60208;

<sup>3</sup>Department of Physics, Trinity College, Dublin, Ireland

Diffusive coarsening is an important mechanism for the evolution of soap froth structure. The growth rate of individual bubbles with  $n$  sides in 2D foams is described by von Neumann's law,  $dA/dt = D(n-6)$ , an exact result. The situation in 3D is much more complicated: the average growth rate of bubbles with  $F$  faces is well described by the approximate relationship,  $V^{-1/3} dV/dt = D(F^{1/2} - F_0^{1/2})$ , where the cross-over  $F_0$  depends on foam polydispersity. The  $F^{1/2}$  behavior is predicted by an analytical theory for bubble geometry based on idealized foam cells called isotropic Plateau polyhedra (IPP), which have  $F$  identical regular spherical-cap faces. IPP theory does not account for dependence of the cross-over on polydispersity, which is evident in Surface Evolver simulations of random foams. We have developed a theory for the cross-over by extending the approach of Glazier and Weaire. The theory is compared to bubble growth rates evaluated from Surface Evolver simulations.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Thursday 11:00 Room 107

SC36

### **Flow characteristics of tailings paste for surface disposal**

David F. James<sup>1</sup>, Minkyung Kwak<sup>2</sup>, and Katherine Klein<sup>2</sup>

<sup>1</sup>Mechanical & Industrial Engineering, University of Toronto, Toronto, Ontario M5S 3G8, Canada;

<sup>2</sup>Civil Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

Mine tailings can be deposited on the surface when highly dewatered, and then the flow characteristics of the tailings paste must be known to predict stack height and extent. To help make predictions, experiments were conducted to relate stack geometry to rheology. Tailings and kaolinite pastes having various water contents were prepared and tested in a laboratory flume-like apparatus to simulate field run-out. At one end of the flume, a fixed volume of paste was released and its final slope was measured. For rheological characterization, the plastic viscosity and yield stress behaviour of each paste were determined using two rheometers, both with vane fixtures to avoid wall slip. Yield stresses obtained at steady state with a stress-controlled rheometer were found to be consistent with end-of-elastic-deformation yield stresses obtained from stress-time profiles with a strain-controlled rheometer. The run-out slope, yield stress, and plastic viscosity all decreased with water content, as expected. The slope was found to increase linearly with yield stress, and slope values were related to yield stress, viscosity and other experimental parameters using the dimensional grouping introduced by Sofra & Boger (2001). Agreement of our data with theirs, using their dimensionless grouping, is reasonable when account is taken of the different definitions of yield stress in the two works.

Thursday 11:25 Room 107

SC37

### **Injection molding of a ceramic suspension: Rheological measurements and computational modeling**

Rekha R. Rao<sup>1</sup>, Thomas A. Baer<sup>1</sup>, Lisa A. Mondy<sup>1</sup>, Laura Halblieb<sup>2</sup>, Anne M. Grillet<sup>1</sup>, and Pin Yang<sup>3</sup>

<sup>1</sup>*Multiphase Transport Processes, Sandia National Laboratories, Albuquerque, NM 871850834*; <sup>2</sup>*Sandia National Laboratories, Albuquerque, NM 87185*; <sup>3</sup>*Sandia National Laboratories, Albuquerque, NM 87185-0959*

Injection molding of a paste of ceramic particles suspended in paraffin wax is used as the basis of a net shape ceramic processing operation. The suspension is highly loaded with the ceramic particles, but a stearic acid surfactant and a polyethylene/polypropylene copolymer plasticizer are used to improve the processability of the material. The paste is injected into the mold creating the green ceramic part with the correct net shape. The wax is then burned out of the green part, which is then sintered to create the final ceramic component. This net shape forming process is agile and inexpensive, since the final part requires no expensive grinding or retooling, thus reducing the manufacturing cycle times and wastes.

Rheological measurements were made in a capillary viscometer for several different temperatures, particle loadings, and shear rates to help understand the flow behavior of the ceramic paste. Two different capillary diameters were used to estimate the effect of slip. The collective data was fit to a temperature-dependent, power-law model using a statistical package that estimates the appropriate parameters of the model to span the temperature and shear rate ranges seen during processing. The wax suspending fluid is shear-thinning at operating temperatures, where it acts more like soft-matter than a liquid. The ceramic suspension shear-thins in a similar manner and shows an Arrhenius-like dependence on temperature and no yield stress.

A finite element model of the injection molding system was developed to provide insights into the filling process, to allow optimization of the die shape and processing variables, and to troubleshoot potential problems such as warping, voids, and inhomogeneities. The modeling uses the optimal parameters from the statistical analysis to look at both two- and three-dimensional simulations of the non-isothermal filling process. The simulations are in turn compared to short shot data.

## **Symposium EM Experimental Methods**

Organizers: Anne M. Grillet and Wesley R. Burghardt

Thursday 8:05 Room 108/109

EM10

### **A novel "cleat" geometry for quantitative rheological characterization of foods and biomaterials**

Charles S. Nickerson and Julia A. Kornfield

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

We present the use of cleated surfaces on parallel disk tools to quantitatively measure the rheological properties of slip-prone foods and biomaterials. Densely-packed protrusions (0.45mm x 0.45mm cross section x 0.6mm length, 0.9mm apart) penetrate the slip layer or tissue, preventing significant flow between cleats. This creates a no-slip boundary ~0.16mm below their tips, which serves as the sample gap boundary - in direct analogy to the parallel plate geometry. This "cleat" geometry overcomes some critical limitations of prior tools intended to suppress slip in these difficult systems (e.g. roughened, vaned, or porous tools): *small sample volumes* may be used, *well-defined shear rates* enable measurements of *absolute rheological data*, and suppression of slip is achieved *without applying significant normal force*. The tools are validated in steady and oscillatory shear over five decades of viscosity ( $10^{-1}$  -  $10^4$  Pa\*s) using a series of Newtonian oils and an entangled polymer melt. The advantage of cleated tools over other slip-prevention methods is demonstrated using an emulsion (mayonnaise), a suspension (peanut butter), and several biological tissues (porcine vitreous humor, cornea, and sclera).

Thursday 8:30 Room 108/109

EM11

**Determination of melt extensional viscosity of polymers and polymer blends with a new elongation fixture for rotational rheometers**Aly J. Franck<sup>1</sup> and Ming Long Yao<sup>2</sup><sup>1</sup>*Marketing, TA Instruments, Alzenau 63755, Germany;* <sup>2</sup>*Software, TA Instruments, New Castle, DE 19720*

Extensional viscosity of a series of polyolefines with varying architecture and composition has been measured using a new melt extensional fixture (EVF) for the ARES rheometer. This fixture can perform uniaxial extension measurements up to a Hencky strain of 4 and elongation rates as high as 30 s<sup>-1</sup>; the maximum temperature is 350°C. The EVF profits from the separation of motor and transducer in the ARES and allows very sensitive force measurements, free of inertia and friction contributions. The molten sample for polymers with low MFI values does not need to be supported, due to the vertical arrangement of the sample. The sample size of 18x10x0.8mm is ideal for characterizing R&D products usually available only in very small quantities. Results for the standard LDPE Lupolen 1810H obtained on the ARES-EVF show excellent agreement with the RME and the original Meissner rotating clamp rheometer.

Results are shown for polyethylene and ethylene vinyl alcohol copolymers. The measured elongation viscosity is analyzed as a function of the degrees of long chain branching for the polyethylenes and the ethylene content for the EVOH copolymers.

Thursday 8:55 Room 108/109

EM12

**Mixing and extensional rheology of bread dough**Trevor S. Ng<sup>1</sup>, Mahesh Padmanabhan<sup>2</sup>, and Gareth H. McKinley<sup>1</sup><sup>1</sup>*Hatsopoulos Microfluids Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139;* <sup>2</sup>*Basic Sciences, Kraft Foods, Glenview, IL 60025*

The rheological behavior of a range of wheat flour dough is examined on the Filament Stretching Rheometer. Specialized end-plate fixtures and protocols were designed and built to ensure consistent preparation and uniform uni-axial extension of the dough samples as well as to minimize the effect of drying.

First, the visco-elastic behavior was studied for a single type of flour, Hard Red Spring (HRS) that was mixed for a constant time (360s) and a water content of 48%. The strain-rate was varied over four orders of magnitude ( $3 \times 10^{-3}$  to  $3 \times 10^0$  s<sup>-1</sup>). We can characterize the measure stress-strain-rate behavior to a reasonable degree of accuracy through a simple non-linear constitutive equation. A single parameter which describes the strain-hardening capability, (a characteristic time  $\tau$ ), can be inferred by fitting experimental results to the equation. We explain the relationship connecting the various parameters to stability against rupture in filament stretching through the Considère Criterion and a linearized analysis originally proposed by Hart.

Thursday 9:20 Room 108/109

EM13

**Validation of a controlled-strain simple shear rheometer for vocal fold tissue characterization**Roger W. Chan<sup>1</sup>, Maritza Rodriguez<sup>2</sup>, and Bokkyu Lee<sup>2</sup><sup>1</sup>*Otolaryngology – Head & Neck Surgery, Biomedical Engineering, University of Texas Southwestern Medical Center, Dallas, TX 75390-9035;* <sup>2</sup>*Biomedical Engineering, University of Texas Southwestern Medical Center, Dallas, TX*

Viscoelastic response of human vocal fold tissues under torsional shear has been reported previously, demonstrating a rheological behavior typical of viscoelastic solid, and shear-thinning viscous behavior under small-strain dynamic shear. However, data have only been obtained at rather low frequencies using controlled stress (up to 15 Hz) and controlled strain (up to 50 Hz) rheometers. In order to characterize the rheological behavior of vocal fold tissues at frequencies of phonation (voice production), a linear simple shear rheometer was built based on the moving magnet linear motor design of an existing material testing system (EnduraTEC ELF 3200). System inertial problems encountered during high-frequency oscillation were minimized by controlled-strain operation, and by fabricating moving parts with light-weight acrylic material. Sensitivity and frequency response of key system mechanical

components were estimated, including an LVDT for strain measurement, and strain gauge and piezoelectric sensors for dynamic force (stress) measurement. The overall frequency response of the rheometer at frequencies of up to 400 Hz was validated by small-amplitude dynamic simple shear experiments conducted on tissue specimens (canine vocal fold mucosa), standard materials (metal beam, silicone), and with no specimen mounted (indication of overall noise of the system). Results of these validation tests suggested that the percentage error of LVDT displacement measurement at 10 to 400 Hz was 7.43% 6.46% (mean and standard deviation). The frequency response of the piezoelectric force transducer was steady (with an error ranging from 0.47% to 2.77%) from 25 Hz to 400 Hz. Overall, the rheometer is capable of quantifying the dynamic viscoelastic properties (magnitude of the complex stiffness) of canine vocal fold tissues up to 200 Hz [Work supported by National Institutes of Health].

Thursday 10:10 Room 108/109

EM14

### **Solving wall slip in parallel disk rheometry data using Tikhonov regularisation**

Sabina Zahirovic<sup>1</sup>, Leong Y. Yeow<sup>2</sup>, David V. Boger<sup>3</sup>, and Franz Grieser<sup>1</sup>

<sup>1</sup>*School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia;* <sup>2</sup>*Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia;* <sup>3</sup>*Particulate Fluids Processing Centre, The University of Melbourne, Melbourne, Victoria 3010, Australia*

The problem of converting the data generated by parallel disk rheometers when wall slip is present into a shear stress-shear rate function and a wall shear stress-slip velocity function is formulated as an integral equation of the first kind. Tikhonov regularization is used to solve this problem. Apart from the two material property functions, the method is also able to obtain an estimate of the yield stress and the critical wall shear stress at which wall slip is first observed. This way of handling parallel disk rheometer data has the advantage that it is independent of the rheological constitutive equation and noise amplification is kept under control by the user-specified parameter in Tikhonov regularization. The performance of this method is demonstrated by applying it to laboratory measurements of highly concentrated water in oil emulsions.

Thursday 10:35 Room 108/109

EM15

### **Testing polymers under supercritical CO<sub>2</sub> using a pressure cell**

Eric F. Brown

*Rheology Division, Anton Paar USA, Ashland, VA 23005*

Supercritical carbon dioxide (CO<sub>2</sub>) is being considered as a polymer solvent during processing. CO<sub>2</sub>, in particular, has found interest because it has low critical temperature, low critical pressure, good solvent properties, and few environmental concerns. We tested a polystyrene melt in our pressure cell to see if a standard concentric cylinder fixture could measure the viscosity of the polymer. The absolute magnitude of the polymer viscosity was lower when exposed to CO<sub>2</sub>; furthermore, the dependence of viscosity on shear rate was steeper.

Thursday 11:00 Room 108/109

EM16

### **Chemorheological degradation of natural rubber at elevated temperatures: Experiments and simulation**

Alan Wineman<sup>1</sup>, John A. Shaw<sup>2</sup>, and Alan Jones<sup>2</sup>

<sup>1</sup>*Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109;* <sup>2</sup>*Aerospace Engineering, University of Michigan, Ann Arbor, MI 48109*

An experimental study of the degradation of a commercial-grade filled natural rubber was conducted. Various temperature histories were investigated for which stress relaxation occurred due to viscoelastic and scission processes. A multi-network model in the framework of finite elasticity will be presented that includes the effects of entropic stiffening, thermal expansion, viscoelasticity, scission, recrosslinking, and oxygen diffusion/depletion. The results of a numerical simulation scheme to predict the mechanical response for arbitrary temperature and stretch histories are compared to uniaxial experimental results.

Thursday 11:25 Room 108/109

EM17

**Combinatorial squeezing-flow array for grading of asphalt**Antonio E. Senador<sup>1</sup>, Montgomery T. Shaw<sup>2</sup>, Patrick T. Mather<sup>3</sup>, and Yatin Patil<sup>4</sup><sup>1</sup>*Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269;* <sup>2</sup>*Department of Chemical Engineering, and Polymer Program, University of Connecticut, Storrs, CT 06269;* <sup>3</sup>*Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106;*<sup>4</sup>*Polymer Program, University of Connecticut, Storrs, CT 06269*

Current specifications for road-paving applications classify asphalts in terms of their end-use temperatures. The rheological measurements used for the classification usually involve annealing steps to ensure that the samples being tested have similar structure as the materials on the road. However, work done by other groups [1] has shown that samples must be isothermally annealed for extended periods (>10 h) prior to rheological measurements, thereby unduly occupying an expensive rheometer. Thus a need exists for a quantitative tool that would allow the rapid measurement of rheological properties of asphalt while allowing long-term thermal conditioning.

In this work, we are investigating the use of a two-dimensional array of circular squeezing-flow elements for classifying asphalt. Each element of the array is a circular disc of material whose diameter is increasing under load. Our array is constructed with a combinatorial arrangement featuring a temperature gradient along one dimension of the array and with the other dimension featuring variation in squeezing force or sample composition, for example. All of the elements are annealed and then tested at the same time, thereby functioning as a parallel rheometer. Using a power-law fluid model for asphalt, the rheological parameters are extracted from the squeezing flow data and then correlated with the measurements obtained from the standard tests. Our presentation will overview the strategy employed, reveal the apparatus design, detail the experimental techniques involved in acquiring element diameter data, and finally present example results with particular attention on selected asphalts.

[1] Summarized in R.E. Robertson, et.al., "Fundamental properties of asphalts and modified asphalts, Vol. 1: Interpretive report, Report No. FHWA-RD-99-212", USDOT Federal Highway Administration, Turner-Fairbank Highway Research Center, 2001.

## Symposium MS Entangled Melts & Solutions

Organizers: Lynden A. Archer and Dimitris Vlassopoulos

Thursday 8:05 Room 111/112

MS27

**Morphology and viscoelastic properties of polystyrene blended with fully condensed polyhedral oligomeric silsesquioxane**Madhu Namani<sup>1</sup>, Hai-Ping Geng<sup>2</sup>, and Andre Lee<sup>1</sup><sup>1</sup>*Chemical Engineering & Material Science, Michigan State University, East Lansing, MI 48824;* <sup>2</sup>*Beijing University of Chemical Technology, Beijing, China*

Polyhedral oligomeric silsesquioxane (POSS) offers a unique approach to examine the effect of molecularly dispersed nanoscopic fillers on rheological properties of entangled polymer melts. Experiments were performed using nearly-monodisperse polystyrene (PS) of varying molecular weights blended with varying amounts of two fully condensed POSS molecules surrounded with phenethyl and styrenyl groups. Due to the chemical similarity between these organic moieties surrounding the silicon-oxygen framework (SiO<sub>1.5</sub>) of POSS and PS, we were able to obtain polymer blends with molecularly dispersed nanoscopic fillers needed to study the effect of intermolecular nanoparticle-nanoparticle interactions and the associated intramolecular interactions on the dynamics of the polymer chains. Differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) were used to characterize the thermal properties and morphologies of the POSS/PS blends. Small-strain oscillatory shear and/or tensile method was used to probe the dynamics of polymer chains of varying chain lengths as influenced by the addition of different chemical moiety of POSS at the glass transition, rubbery state and the terminal-flow transition regions. The effect of time on the interactions between polymer-particle and particle-particle has been studied through aging experiments. Results obtained from the thermal and mechanical

characterization methods were compared with morphological observations to better understand the structure-property relationship of polymers containing molecularly dispersed nanoscopic fillers.

Thursday 8:30 Room 111/112

MS28

**Effects of functionalized nanoparticles on the morphology of polystyrene-block-polybutadiene-block-polystyrene (SBS) triblock copolymers**

Daniel B. Drazkowski and Andre Lee

*Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824*

Block copolymers have received significant research interest over the past several decades for their ability to form self-assembled microstructures. The architecture of this self-assembled morphology has applications in nanotechnology along with profound effects on material properties. By adding functionalized nanoparticles to the copolymer systems the compatibility between constituent blocks can be modified thus changing the self-assembled morphology. In this study, we examine the effect of adding polyhedral oligomeric silsesquioxane (POSS), an inorganic silicon-oxygen cage structure with organic moieties bonded to the silicon atoms, into a matrix of polystyrene-block-polybutadiene-block-polystyrene (SBS) triblock copolymers. Not only can POSS functionality be readily modified, the addition of POSS can be done by physically blending individual POSS molecules or by chemically attaching the POSS to the copolymer backbone. Thus, the amount, type, and method of addition of the POSS molecules give added control to the self-assembled microstructure. Small amplitude oscillatory shear experiments were used to characterize the stability of the morphology with increasing temperature via order-disorder transition temperature (ODT) and to examine rheological responses of the melt for each system. Small angle x-ray scattering (SAXS) experiments were used to supplement the rheological ODT characterization and to examine the effect of POSS type and addition method on the copolymer morphology. Dynamic mechanical testing was also used to inspect POSS effects near the glass transition temperature. The effects of organic moiety of POSS and the method of incorporation are discussed.

Thursday 8:55 Room 111/112

MS29

**Scaling relations for shear-induced isothermal crystallization of poly(butene-1) samples**

H. Martin Laun<sup>1</sup>, Chitiur Hadinata<sup>2</sup>, Max Ruellmann<sup>2</sup>, and Claus Gabriel<sup>1</sup>

<sup>1</sup>*Polymer Physics, BASF Aktiengesellschaft, Ludwigshafen/Rhein 67056, Germany;* <sup>2</sup>*BASF Aktiengesellschaft, Ludwigshafen/Rhein, Germany*

Isothermal crystallization in continuous shear flow of three grades of PB-1 having different molecular weights and breadths of the MWD was investigated by means of rotational and capillary rheometry covering a shear rate range of 0.0001 up to 500 1/s and temperatures between 99°C and 107°C. The up-shoot in viscosity after a certain time is used to define an onset time for both quasi-quiescent and shear-induced crystallization. A temperature invariant mastercurve is obtained for each material if the ratio of measured and quasi-quiescent onset time is plotted versus the product of shear rate and square root of the quasi-quiescent onset time. Possible reasons for that behaviour will be addressed. The existence of a material-specific mastercurve considerably simplifies the characterization of the effect of molecular structure on the crystallization behaviour. An additional multiplication of the abscissa by the square root of the characteristic retardation time of the melt, finally yields a dimensionless representation of the mastercurve. The latter is suited to define the threshold value of the shear rate for the occurrence of shear-induced crystallization, independent of the breadth of the MWD. The underlying morphologies as studied by a Linkham hot shear stage will be addressed.

Thursday 9:20 Room 111/112

MS30

**Modeling flow-enhanced crystallization in fiber spinning**

Anthony J. McHugh, William Kohler, and Prashant Shrikhande

*Chemical Engineering, Lehigh University, Bethlehem, PA 18015*

A feature of fiber spinning of crystallizable polymers that plays a controlling role in the evolution of properties is the occurrence of flow-enhanced crystallization (FEC). A major challenge in modeling this process is capturing the phenomenon of necking at high spin speeds which is directly related to the coupling of viscoelasticity in the system with crystallization along the spinline. Our approach involves the use of separate constitutive equations for the two phases: melt and semi-crystalline. Since our models are microstructurally based they allow coupling of fiber

structure (crystallinity and orientation) with the macroscopic stress, velocity, and temperature fields. This talk will emphasize recent work modeling the melt spinning of PLA fibers in which the melt phase is treated in terms of the extended pom-pom model which allows accounting for entanglement effects. A challenge with this system is to incorporate the formation of a high temperature co-crystal phase that forms in the high-speed spinning of racemic mixtures of L and D PLA. Comparison with experimental data will be shown.

Thursday 10:10 Room 111/112

MS31

### **Kinetics in melting of polymers: A route to new state of melt**

Sanjay Rastogi<sup>1</sup>, Dirk Lippits<sup>1</sup>, Gerrit Peters<sup>2</sup>, and Han Meijer<sup>2</sup>

<sup>1</sup>*Chemical Engineering, Eindhoven University of Technology, Eindhoven, North Brabant 5600MB, The Netherlands;* <sup>2</sup>*Mechanical Engineering, Eindhoven University of Technology, Eindhoven, North Brabant 5600MB, The Netherlands*

We demonstrate that, unlike in inorganic materials, melting of polymers can be very different for the same material. The study performed on Ultra High Molecular Weight Polyethylene (UHMW-PE) proves that melting depends on the polymer chain length and the crystal topology, the latter being mainly determined by the synthesis and crystallization conditions. For a highly disentangled polymer that can be obtained by controlled synthesis, where ultimately single chains form single crystals, the resulting melt state strongly depends on the kinetics involved in the melting process. By controlling the thermal history, different melt states with pronounced differences in the rheological and crystallization behavior can be generated. When nascent crystals, obtained on synthesis, are given sufficient time to melt below the normally observed melting temperature (141°C), a heterogeneous melt state is formed with an inhomogeneous distribution of topological constraints - leading to a distribution of more entangled and less entangled (disentangled) domains. The topological constraints are rather unique in the sense that reptation of chains, required for the homogenization of the entanglement distribution, is limited, even after leaving the UHMW-PE melt for several hours at temperatures as high as 180°C. One of the striking effects of the heterogeneous melt is a considerable decrease of the plateau modulus when compared to a normal melt with homogeneously distributed entanglements. Other unique features are a high crystallization rate (more than a decade higher when compared with a normal melt) and easy solid-state ultra drawability on crystallization from the heterogeneous melt (with draw ratio larger than 30, which is at least 3 times higher than solids crystallized for a normal melt). These findings suggest that the heterogeneous melt is a, until now, unknown state of melt in which the chain conformations obtained by a controlled, special melting route is not the same as the normal, equilibrium, homogeneous melt state.

Thursday 10:35 Room 111/112

MS32

### **In situ measurements of molecular orientation in commercial thermotropic liquid crystalline polymers in transient shear flows**

Stanley Rendon<sup>1</sup>, Wesley Burghardt<sup>1</sup>, and Robert Bubeck<sup>2</sup>

<sup>1</sup>*Northwestern University, Evanston, IL;* <sup>2</sup>*Michigan Molecular Institute, Midland, MI*

Despite significant advances in the understanding of dynamics of lyotropic liquid crystalline polymer (LCP) solutions, and 'model' thermotropic LCP melts characterized by flexible backbone spacers and lower transition temperatures, there is only limited fundamental understanding of commercial main-chain thermotropic LCPs. A major stumbling block is limited physical and chemical stability at the high melt temperatures of commercial LCPs which has to date rendered fundamental 'monodomain' studies impossible, and which creates well-documented complications even for conventional shear rheometry. As a result, it is not directly established whether commercial thermotropes are of the shear-tumbling or shear-aligning classification, the most basic information necessary to rationally anticipate how flow during processing might impact structure development. Instead, only indirect evidence is available, which tends to support the hypothesis of tumbling. In more idealized materials, direct measurements of molecular orientation in transient shear flows (reversals, step-changes and flow cessation) have often shed light on the underlying director dynamics. Here we report attempts to apply such methodology to two commercial thermotropic LCPs (Vectra A950 and B950). Synchrotron x-ray scattering in conjunction with a high speed area detector provides sufficient time resolution to limit the total time spent in the melt during testing, while further modifications to an x-ray capable shear cell provide a more robust platform for working with LCP melts at high temperatures. The transient orientation response to changes in flow condition do not yield definitive signatures of either tumbling or alignment. However, Vectra A shows clear responses to step-increase or step-decrease in shear rate, which contrasts with expectations and experience with shear-aligning nematics. Interestingly, these two

polymers show opposite trends in orientation following flow cessation, which appears to correlate with evolution of dynamic modulus.

Thursday 11:00 Room 111/112

MS33

**Modeling of the shear-induced isotropic-to-nematic phase transition of side chain liquid-crystalline polymers**

Siegfried Hess and Patrick Ilg

*Institute for Theoretical Physics, Technische Universität Berlin, Berlin, Berlin D - 10623, Germany*

The shear-induced isotropic-to-nematic phase transition of side chain liquid-crystalline polymers is studied theoretically. A modification of previous models of main-chain liquid crystals to the case of side chain liquid-crystalline polymers is proposed. Orientational and rheological properties of the model are studied in plane shear flow. It is found that the coupling of the mesogenic side chains to the polymer back bone modifies the dynamical properties considerably. For example the shear-induced isotropic-to-nematic transition is shifted compared to ordinary nematics and liquid crystals. Due to the different relaxation times of the side chains and the polymer back bone, a stress plateau is observed. Results for different temperatures all within the isotropic regime are shown. Close to the transition temperature, the shear stress is found to decrease with increasing shear rate for certain intervals of shear rates, indicating a mechanical instability. We expect that in this regime shear banding occurs in spatially homogeneous systems. Predictions of the present model agree qualitatively with experimental results [C. Pujolle-Robic, L. Noirez, Nature 409, 167 (2001)].

Thursday 11:25 Room 111/112

MS34

**Non-linear dynamics in side-chain liquid crystal polymers**

Laurence Noirez

*Laboratoire Léon Brillouin (CEA-CNRS), Saclay, France*

Flow induced phase transitions are some of the most spectacular but also less explained non-equilibrium phenomena. Their understanding is of practical importance for tuning the processing conditions for plastics, petroleum products, and other related materials. Side-Chain Liquid Crystal Polymers (LC-polymers) have undergone extensive investigation since they were synthesised [1], however, shear-induced transitions in these melts is only very recent identified [2]. At  $T > T_{NI}$ , and above a critical shear rate, the isotropic phase transforms to a non-equilibrium nematic phase. This non-equilibrium phase is singular, illustrating that shear-induced phenomena are not describable as a simple shift of the Isotropic-Nematic transition temperature. The origin of this very spectacular non-linear behaviour is unknown. Because it is an unexpected phenomenon and because of their well-characterised physico-chemistry properties, LC-polymers are excellent molecule tools for the understanding of non-linear phenomena. We will determine and compare the characteristic times of a LC-polymer system to the critical times associated with the shear induced phase. It will be demonstrated that shear induced transitions cannot be simply coupled with orientational-order fluctuations or with the viscoelastic terminal time, leading us to consider and to identify longer time scales.

# Poster Session

## Symposium PO Poster Session

Organizer: Patrick T. Mather

Wednesday 6:00 Lubbock Memorial Civic Center

PO1

### **Development of a microfluidic rheometer for measuring the complex modulus and complex viscosity of complex fluids**

Jai A. Pathak and Kathryn L. Beers

*Polymers Division, NIST, Gaithersburg, MD 20899-8544*

The measurement of the rheology of complex fluids at the micro-scale is an important scientific and technical challenge in the evolving field of microfluidics. As part of the ongoing effort at the NIST Polymers Division to integrate synthesis of model polymers and the characterization of their physical chemistry and rheology on a lab-on-a-chip platform, we present results of our work on the development of a microfluidic rheometer based on the well-established metrology principle of magnetic particle rheometry. We are inspired by ideas from the bio-rheology field, with which we face a common experimental challenge: the availability of extremely small quantities (tens of  $\mu\text{L}$ ) of fluid samples. We will discuss the design and fabrication of the instrument, and present results of oscillatory and steady shear rheometry on diverse fluids, including standards of known viscosities and a plethora of complex fluids.

Wednesday 6:00 Lubbock Memorial Civic Center

PO2

### **Rheological behavior of waterborne polyurethane dispersions**

Samy A. Madbouly, Joshua U. Otaigbe, Ajaya K. Nanda, and Douglas A. Wicks

*School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406*

The rheological behavior of waterborne polyurethane dispersions was investigated with small amplitude oscillatory shear flow experiments over wide ranges of concentration, degree of neutralization, chain extension and temperatures to accelerate efforts to understand their film formation characteristics. The rheological properties of these environmentally-friendly dispersions were found to be dependent on composition and degree of postneutralization. But the chain extension and degree of preneutralization were observed to have little effect on the rheological behavior of the dispersions at a constant concentration. The complex viscosity of the polyurethane dispersions increased dramatically at a critical concentration of polyurethane (40 wt%) below which the viscosity increased slightly with composition. At this critical concentration the particles are very crowded and the observed viscosity increase is associated to the hydrodynamic interaction between the different particles. With increasing degree of postneutralization the viscosity increases greatly due to the increase in the particle size and the decrease in the free volume. The rheological behavior of the polyurethane dispersions was also studied at different temperatures up to 70 °C. The data obtained was well described by the Cross model and WLF superposition principle. At temperatures higher than 70 °C, the rheological behavior was changed dramatically and the WLF superposition principle failed to represent the behavior.

Wednesday 6:00 Lubbock Memorial Civic Center

PO3

**Gelation kinetics of waterborne polyurethane dispersions studied by rheometric methods**

Samy A. Madbouly, Joshua U. Otaigbe, Ajaya K. Nanda, and Douglas A. Wicks

*School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406*

Thermal induced gel formation for polyurethane dispersions has been detected rheologically. The possibility for the formation of a three-dimensional polymer network in the polyurethane dispersions was found to be composition dependent. The higher the concentration of polyurethane, the higher the possibility for gelation. The linear viscoelastic properties of the polyurethane dispersions were found to be greatly changed by the onset of the gelation process. The viscoelastic material functions, such as dynamic shear moduli,  $G'$  and  $G''$ , complex shear viscosity,  $\eta^*$  and loss tangent,  $\tan\delta$  were found to be very sensitive to the structure changes during the gelation process and the formation of a three-dimensional polymer network. At the onset temperature of the gel formation, an abrupt increase in  $G'$ ,  $G''$  and  $\eta^*$  by several orders of magnitude during the dynamic temperature ramps (2 °C/min heating-rate) was observed. Isothermal time evolution measurements at different constant temperatures (55, 60, 65 and 70 °C) over a wide range of frequency for the gelation process of the polyurethane dispersions were also investigated. The gel point,  $t_{gel}$ , evaluated from the point of intersection in  $\tan\delta$  versus curing time obtained at different constant shear frequencies, where is no longer frequency dependent and all curves crossover indicating the validity of Winter-Chambon criterion. The value of  $t_{gel}$  obtained from the coincidence of  $G'$  and  $G''$  was almost equal to that determined from  $\tan\delta$  versus  $t$ .

Wednesday 6:00 Lubbock Memorial Civic Center

PO4

**Crossing dynamics of surfactant threadlike micelles**

Satoru Yamamoto and Shi-aki Hyodo

*Computational Physics Lab., Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan*

A dissipative particle dynamics simulation was applied to study the crossing dynamics at an entanglement point of surfactant threadlike micelles in an aqueous solution. In this study, the possibility of a phantom crossing, which is the relaxation mechanism for the pronounced viscoelastic behavior of surfactant threadlike micellar solution, was investigated. A surfactant is modeled by connecting coarse-grained particles that represent the hydrophilic head and hydrophobic tail groups. A threadlike micelle was stabilized with moderate repulsive forces between hydrophilic parts of surfactants. When two threadlike micelles were encountered, a phantom crossing reaction occurred occasionally after fusion at an entanglement point, or one micelle was cut down at a branch point. Increasing repulsive forces between hydrophilic parts of surfactants, fusion occurred less and a threadlike micelle was frequently broken down at an entanglement point before fusion. In these three schemes (a phantom crossing, cut down at the branch point, and break down at the entanglement point), the breakage occurs at somewhere along the threadlike micelle. The breakage is considered as an essential process in the relaxation mechanism, and a phantom crossing can be seen as a special case of this process.

Wednesday 6:00 Lubbock Memorial Civic Center

PO5

**Strain hardening occurrence in uniaxial elongational viscosity by addition of a small amount of PTFE nanofiber**Takashi Kurose<sup>1</sup>, Tatsuhiro Takahashi<sup>2</sup>, and Kiyohito Koyama<sup>2</sup>*<sup>1</sup>Venture Business Laboratory, Yamagata University, Yonezawa, Yamagata 992-8510, Japan; <sup>2</sup>Yamagata University, Yonezawa, Yamagata 992-8510, Japan*

The property about the uniaxial elongational viscosity of the blend consisting of polycarbonate (PC) and a small amount of polytetrafluoroethylene (PTFE) has been studied. The blends were prepared with a twin-screw kneader at 280°C. The structural observations of the fracture cross-section of the blend sample were performed with SEM. It was clearly observed that PTFE fibril less than 100nm in a diameter was generated by kneading with molten PC, and dispersed relatively uniformly in PC matrix. Uniaxial elongational viscosity of blends showed stronger the strain-hardening by presence of PTFE fibrils. The mechanism of the occurrence of the strain-hardening was investigated. Blend sample showed large strain recovery after uniaxial elongation. In the SEM observation of the blend sample after elongation and after strain recovery, it was observed that the diameter of PTFE fibrils became thicker during the strain recovery. WAXD pattern also showed that the crystal chain of PTFE in the PTFE fibril orientated along an

elongational direction. These results support that fibrillated PTFE in blend sample are stretched during elongation, the strain-hardening property should be attributed to the restoring force of PTFE fibrils.

Wednesday 6:00 Lubbock Memorial Civic Center

PO6

**Transient behavior of Boger fluids under extended shear flow in a cone-and-plate rheometer**

Veronica M. Calado<sup>1</sup>, James M. White<sup>2</sup>, and Susan J. Muller<sup>3</sup>

<sup>1</sup>*Escola de Química - Centro de Tecnologia, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil;* <sup>2</sup>*CEB 221, General Electric Global Research, Niskayuna, NY 12309;* <sup>3</sup>*Department of Chemical Engineering, University of California, Berkeley, Berkeley, CA 94720-1462*

Three different dilute solutions of high molecular weight polymers in viscous, binary solvents were used in experiments performed in a cone-and-plate rheometer. The solutions all fall into the class of fluids referred to as "Boger fluids" and were previously used in studies of viscoelastic Taylor-Couette instabilities. Under prolonged shearing in the cone-and-plate geometry, these fluids all exhibited a decrease of the first normal stress growth function  $N_{1+}(t)$  from an initial plateau value to a second, lower plateau value. This behavior has been previously observed, but is here reported for widely used polyisobutylene-based Boger fluids for the first time. As in earlier studies, the time at which this decrease occurs (the decay time) is much longer than the polymer molecule's relaxation time. Here, we focus on three issues: 1) the time-temperature superposition of the first normal stress growth function  $N_{1+}(t)$ , including the decay time and the value of the second plateau, 2) the sample recovery time required to reproduce the initial plateau value of  $N_{1+}$  and the decay time, and 3) the relationship between the time scales for this decay of normal stresses and the onset of viscous heating induced instabilities in the Taylor-Couette geometry. Our results suggest that shear-induced conformational changes, possibly coupled to viscous heating of the sample, may be responsible for the decrease in the first normal stress growth function during prolonged shearing.

Wednesday 6:00 Lubbock Memorial Civic Center

PO7

**Apparent mass uptake measurements in thin polymer films using a quartz crystal microbalance: Errors induced by film expansion stresses**

Lameck Banda, Mataz Alcoutlabi, and Gregory B. McKenna

*Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121*

We describe part of a continuing investigation into the structural recovery of polymer glasses subjected to plasticizer-jumps; relative humidity (RH) and carbon dioxide pressure (PCO<sub>2</sub>). The study uses frequency change measurements induced in a quartz crystal onto which is deposited a thin film of a polymer glass. Prior work using volume measurements showed that the structural recovery phenomenon after plasticizer concentration-jumps is qualitatively similar to results obtained after temperature jumps, but quantitatively different. Here we examine the frequency changes on the quartz crystal following RH and PCO<sub>2</sub> changes. The findings are significant for two reasons: they successfully demonstrate the study of the structural evolution of a polymer glass subjected to plasticizer-jumps by the real-time monitoring of frequency change in the crystal. Importantly, a significant fraction of the frequency change is induced by the mechanical stresses in the crystal due to expansion or contraction of the film coating. This is observed to be true even for relatively thin films. These results are significant because, though the quartz crystal microbalance has been used as a force transducer and mass sensing device for a long time, there appears to be a lack of attention to response of the crystal to mechanical stresses when the QCM is used as a mass sensing device. This is particularly important for measurements involving glassy polymers because significant stresses can be induced in these materials due to sorption and desorption of gases and other diluents. We discuss errors in mass uptake measurement that can be over 25% of the total signal due to stresses induced in the quartz crystal by the swelling or thermal expansion mismatch between the polymer film and the more dimensionally stable crystal.

Wednesday 6:00 Lubbock Memorial Civic Center

PO8

**Edge effects from imperfect loadings (excess or deficit) in rotational parallel plate rheometry**David W. Giles<sup>1</sup> and Russell W. Hooper<sup>2</sup><sup>1</sup>*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455;* <sup>2</sup>*9233 Computational Sciences, Sandia National Laboratories, Albuquerque, NM 87185*

In rotational parallel plate rheometry, the ideal sample shape is a cylindrical disk with axially straight sides and a diameter equal to that of the plates. It can be difficult to achieve this in practice. For example, a high viscosity or elasticity can make loading or "trimming the edge" problematic and some sample may protrude beyond the edge of the plates or be pulled out from between them. A minor excess or deficit can have a larger effect than might be appreciated. The error can easily exceed 10% for a typical geometry of 1 mm gap and 25 mm diameter, for example, and increases at least linearly with the gap to radius ratio. Vrentas et al. (1991) first reported on this error for a "plate and cup" geometry, Macosko (1994) summarized their results and fit them to a simple equation for easy estimation of the error, and we presented results at the 71st Annual Meeting of this Society (1999), extending applicability. We now present new results for a variety of geometries common in practice, including plate and cup (sea of fluid), bulbous excess or deficit, capped disk, and minimally wetted larger lower plate. We compare numerical and analytical results for the viscosity measurement of a Newtonian liquid, and experimental results obtained from small-strain sinusoidal oscillation tests of linear viscoelastic materials. Good agreement is found, and we present simple equations for easy estimation of the error based on geometry type, a parameter describing the amount of excess, and the gap to radius ratio.

Wednesday 6:00 Lubbock Memorial Civic Center

PO9

**Interfacial tension errors in the Cohen and Carriere analysis of fiber retraction**

Sachin Velankar and Jeffrey Martin

*Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261*

The Imbedded Fiber Retraction method is a popular means of measuring the interfacial tension between two immiscible polymers. In this method, a short fiber of one polymer (length/diameter ratio ranging from about 3-15) is imbedded in a matrix of the other polymer. Upon melting, interfacial tension drives retraction of the fiber into a spherical shape. The rate of this retraction can yield the interfacial tension.

Implementation of the method requires that the experimentally-measured retraction be fitted to a model of the retraction using the interfacial tension as the fitting parameter. The approximate model of Cohen and Carriere (CC), originally proposed when the retraction method was first developed, is still commonly used for this purpose. In contrast, a later model developed by Tjahjadi, Ottino and Stone (TOS) has not found common usage. We compare these two methods experimentally. The key feature of our experiments is the use of a spinning drop tensiometer to generate the elongated fibers. This enables us to measure the equilibrium interfacial tension immediately prior to fiber retraction, thus allowing rigorous evaluation of the retraction models.

We demonstrate that the CC model gives large errors in the interfacial tension when the viscosity of the fiber exceeds that of the matrix polymer. In contrast, the equilibrium interfacial tension from the TOS model agrees well with the equilibrium interfacial tension for all cases studied. Furthermore, the TOS model is easier to implement experimentally, and is theoretically rigorous. In summary, we recommend that the CC model be avoided in favor of the TOS model when analyzing fiber retraction experiments

Wednesday 6:00 Lubbock Memorial Civic Center

PO10

**Rheological behavior of oligoimide/clay nanocomposite dispersions**Gilles M. Divoux<sup>1</sup>, Vladimir E. Yudin<sup>2</sup>, and Joshua U. Otaigbe<sup>1</sup><sup>1</sup>*School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406-0076;* <sup>2</sup>*Russian Academy of Sciences, Institut of Macromolecular Compounds, Saint Petersburg 199004, Russia*

The rheological behavior of novel aromatic oligoimides based on 2, 2 bis[4-(4-aminophenoxy) phenyl]sulfone and 1,3-bis(3, 3',4 ,4' -dicarboxyphenoxy)benzene with phthalic anhydride as end groups filled with clay nanoparticles were studied under both steady and small strain oscillatory shear flows as functions of molecular weight, glass

transition temperature, processing conditions and surface chemical treatment of the clay particles. As expected, the viscoelastic material functions were found to be strongly dependent on these experimental variables and on the intrinsic particle-matrix and particle-particle interactions in the oligoimide/clay nanocomposite dispersions. The magnitude of the storage and loss moduli increased by about one order of magnitude at high temperature with increasing concentrations of the clay up to 8 wt.%, showing dramatic changes near the glass transition temperatures of the oligoimides. The temperatures corresponding to the maximum relaxation processes depicted by the rheological data were found to be in good agreement with those obtained from differential scanning calorimetric measurements. This study confirmed that rheometry is a reliable method for probing the structure-property evolution in these materials, making it possible to prepare oligoimide/clay nanocomposite dispersions with prescribed macromolecular structure and function and rheological properties. The oligoimide/clay dispersions of this study show promise as useful precursors to polyimide films that provide tunable responses to external stimuli such as deformation, flow and temperature that are common in polymer film and coating applications.

Wednesday 6:00 Lubbock Memorial Civic Center PO11  
**Evaluating the effectiveness of processing techniques for PP nanocomposites through rheology**

Michail K. Dolgovskij and Christopher W. Macosko

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

Polypropylene (PP) nanocomposite blends have been prepared using three melt blending techniques, batch twin-screw blending, traditional twin-screw extrusion, and multilayer coextrusion. The blends contained one of two grades of PP (either extrusion grade or injection molding grade), PP-g-MA, and organically modified montmorillonite clay. Melt rheology was then used to probe the extent of dispersion of the nanoclay filler for each preparation method. The evolution of a solid-like plateau in the elastic modulus  $G'$  was indicative of a dispersed network of clay platelets, and the relative magnitudes of these plateaus were used to assess the effectiveness of the dispersion method. Additionally, results from transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) experiments reassured our assessment.

Wednesday 6:00 Lubbock Memorial Civic Center PO12  
**Case study: Vane rheometry superiority over smooth disk geometry in evaluating rubber-particle-filled asphalt emulsions as cold-patch sealants**

David J. Moonay

*Brookfield Engineering Labs., Inc., Middleboro, MA 02346*

A crumb-rubber-filled asphalt emulsion met a specification of 2,500-20,000 mPa·s as measured by Brookfield RVT viscometer with RV-6 disk-shaped spindle at 10 rpm. However, it was subsequently found that this material could not be pumped from the delivery trucks at the jobsite. We, therefore, analyzed the material by several different methods in order to find an improved test procedure that would provide more meaningful data. All experiments were performed at 20-23 °C. RVDV-III+ rheometer measurements with RV-6 spindle at 10 rpm gave a mean average maximum apparent viscosity or  $\eta_{am} = 12,780 \pm 1896$  mPa·s.  $\eta_{am} = 77,108 \pm 4082$  mPa·s measured by HBDV-III+ with V-72 vane spindle at 5 rpm and  $\eta_{am} = 80,201 \pm 11,631$  mPa·s with V-71 vane at 2.5 rpm. Thixotropy was further confirmed by speed-ramp measurements with the HBDV-III+/V-72 system. The average yield stress, measured with HBYR-1 Yield Rheometer and V-72 spindle at 5 rpm, was  $\tau_{y,ave} = 46.14 \pm 1.76$  Pa. Controlled Stress experiments were performed with a Brookfield R/S-SST rheometer and V80-40 vane. Yield stresses were measured with a 0-200 Pa stress ramp over 100 s;  $\tau_{y,ave} = 31.90 \pm 4.43$  Pa. In conclusion, vane rheometry methods are superior to the specification's procedure in analyzing crumb-rubber-filled asphalt emulsions because: (1) vane spindles test the heterogeneous, solid-filled material as a whole, whereas the disk primarily tests the liquid emulsion matrix and, therefore, (2) vane-method viscosities, approximately six times higher than those of the specified method, far more realistically describe the material's application behavior and (3) the specification's method essentially ignores the significant yield stress of the multiphase sample.

Wednesday 6:00 Lubbock Memorial Civic Center

PO13

**The impact of nanoconfinement, surfaces and interfaces on the structural relaxation of polymeric glasses monitored on the molecular-scale by fluorescence**Rodney D. Priestley, Linda J. Broadbelt, and John M. Torkelson*Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208*

Polymers confined to nanoscopic geometries have shown a substantial deviation in the glass transition temperature ( $T_g$ ) relative to that of the bulk material. How these deviations in  $T_g$  alter the structural relaxation of polymeric glasses confined to nanoscopic geometries has emerged as a key question that needs to be addressed for both scientific and technological reasons. Here the effect of nanoconfinement, surfaces and interfaces on structural relaxation of glassy polymers is investigated.

The effect of nanoconfinement on physical aging of polystyrene (PS) and poly(methyl methacrylate) (PMMA) has been studied using fluorescence. Thin (500-nm-thick) and ultrathin (20-nm-thick) films supported on silica were annealed above and below the bulk glass transition temperature ( $T_g$ -bulk). With PMMA, which has attractive polymer-substrate interactions, ultrathin films exhibited aging at  $T_g$ -bulk + 7 K while thin films did not. With PS, which lacks polymer-substrate interactions, thin films exhibited physical aging at  $T_g$ -bulk - 10 K while ultrathin films did not. Deep in the glassy state of PMMA, much less structural recovery was observed in ultrathin films than in thin films. Additionally, the temperatures of maximum and minimum aging rates were strongly affected by confinement in PMMA.

The effect of surfaces and interfaces on physical aging of PMMA was also investigated using fluorescence. The ability to monitor structural relaxation at specific distances from a substrate or interface was accomplished using multi-layer films with fluorescence probes placed in specific layers. Retarded structural relaxation was observed in PMMA at both the air-polymer interface and the silica substrate, with the latter having the greatest impact on structural relaxation. The effect of the silica substrate and air-polymer interface was observed to perturb structural relaxation several tens of nanometers into the bulk of the film.

Wednesday 6:00 Lubbock Memorial Civic Center

PO14

**Surface gelation of beta-casein**Grigor B. Bantchev<sup>1</sup> and Daniel K. Schwartz<sup>2</sup>*<sup>1</sup>Chemistry, Louisiana State University, Baton Rouge, LA 70802; <sup>2</sup>Dept. of Chemical & Biological Engineering, University of Colorado, Boulder, CO 80309-0424*

A magnetic rod interfacial shear rheometer was used to measure the properties of beta-casein adsorbed at the air/solution interface as a function of aging time. Over a wide range of concentrations ( $1 \times 10^{-6}$  to  $2 \times 10^{-2}$  wt % beta-casein) the initial rheology of the adsorbed surface layer is dominated by a viscous response of the interface. For solutions in the range  $5 \times 10^{-3}$  to  $2 \times 10^{-2}$  wt %, interfacial gelation is observed after ~15 h of aging, long after the surface tension has stabilized. In particular, although both components of the complex interfacial shear modulus (i.e., the storage and loss moduli) gradually increase with aging time, the ratio of the loss to the storage modulus-the loss tangent-decreases and drops below unity. The frequency dependence of the shear modulus is consistent with sol-gel transitions observed in bulk systems and described within the context of percolation theory. Adsorbed layers were transferred to solid supports and imaged by atomic force microscopy. The aging of the layer was accompanied by the formation of distinct disk-shaped protein nanoparticles (~20 nm in diameter). Under conditions where a gelled layer was expected, we observed ordering of the particles and the formation of elongated aggregates or linear rows. The Brewster-Angle Microscopy (BAM) images were also obtained during the adsorption and gelation processes and during the degradation of the protein layer following addition of the surfactant sodium dodecyl sulfate (SDS). If SDS was added prior to interfacial protein gelation, the layer developed a foamlke morphology consistent with a fluid interfacial protein layer. However, if SDS was added after gelation, the protein layer was observed to fracture, consistent with the behavior of a solid phase.

Wednesday 6:00 Lubbock Memorial Civic Center PO15

**Multi correlator fiber-optics dynamic light scattering apparatus**

Grigor B. Bantchev, Paul Russo, and Robin L. McCarley  
*Chemistry, Louisiana State University, Baton Rouge, LA 70803*

Dynamic Light Scattering (DLS) is a useful, non-invasive technique. We report the construction of a multi-angle, multi-correlator apparatus for simultaneously observing several (up to 8) channels. It can be used to study microrheology of gels or other composite systems. Demonstration experiments are made with Teflon (tracer) particles in aqueous polyethylene oxide (matrix). We can measure the translational diffusion coefficient of the tracer particles, at various scattering vectors, which follows the microrheology of the system. The measurement of depolarized signal holds the promise that both the translational and the rotational diffusion coefficients of the tracer particles can be obtained quickly.

Wednesday 6:00 Lubbock Memorial Civic Center PO16

**Ballistic performance and squeeze-flow characterization of STF's reinforced by short discontinuous fibers**

Caroline H. Nam<sup>1</sup>, Matthew J. Decker<sup>1</sup>, Christopher Halbach<sup>1</sup>, Eric D. Wetzel<sup>2</sup>, and Norman J. Wagner<sup>1</sup>  
<sup>1</sup>*Department of Chemical Engineering, University of Delaware, Newark, DE 19716;* <sup>2</sup>*Army Research Laboratory, Aberdeen, MD 21005*

Colloidal shear thickening fluids (STFs) reinforced with short discontinuous fibers are shown to exhibit novel behavior under ballistic performance testing and squeeze-flow rheology. Fiber properties such as length distribution, rigidity, and aspect ratio are studied at various concentrations, utilizing a range of fiber materials such as carbon fibers, glass fibers, and high-density polyethylene fibers. Ballistic performance is tested using fragmentation simulating projectiles (FSPs) by comparing depth of penetration into a clay witness. Significant differences in penetration resistance are observed for different STF-fiber composites, with some composites allowing only minimal penetration by the FSP. These ballistic performance results correlate well with results from squeeze-flow characterization, suggesting a relationship between viscous stress transfer and penetration resistance.

Wednesday 6:00 Lubbock Memorial Civic Center PO17

**A new pressurizable dilatometer for measuring the time-dependent bulk modulus of polymers**

Yan Meng, Paul A. O'Connell, Gregory B. McKenna, and Sindee L. Simon  
*Chemical Engineering, Texas Tech University, Lubbock, TX 79409*

A new piston-cylinder-type pressurizable dilatometer controlled by a stepper motor has been developed which enables measurement of the time-dependent bulk modulus and compliance of viscoelastic materials. Investigation of the bulk modulus of thermosets is particularly of interest because this function is important for predicting the isotropic residual stress development during the cure of thermoset-reinforced composites. In addition, we plan to perform studies elucidating whether the molecular origins for the bulk and for the shear responses are the same. The design of the instrument and initial calibration results will be presented.

Wednesday 6:00 Lubbock Memorial Civic Center PO18

**A new phenomenological rheology model to interpret oscillatory shear data**

Charles P. Lusignan  
*Research and Development, Eastman Kodak Company, Rochester, NY 14650-2109*

It is useful to represent oscillatory shear data with an analytical model containing a few meaningful parameters. The Havriliak-Negami (HN) model is the complex analogue of the Carreau-Yasuda (CY) viscosity function, thus it can fit both the storage and loss moduli as functions of frequency. Models of this type achieve their data fitting flexibility by introducing an empirical exponent 'a' that produces a broad crossover to the high frequency power-law response 'n'. The n and a exponents have values between 0 and 1, and are nonlinearly coupled to the single relaxation time.

Unfortunately, this approach has several limitations: (1) It is difficult to verify the uniqueness of the parameter estimates because of the parameter coupling; (2) To approximate the crossover to the rubbery plateau and reduce the number of free parameters one often sets  $n$  to some small value; (3) The low-frequency storage modulus scales as  $\log(G') \sim (1 + a) \log(\omega)$ . The correct terminal response is recovered only if  $a = 1$ , but then the model's ability to fit experimental data is drastically reduced.

We develop a new 5-parameter model that retains much of the spirit of the HN equation, but one that also has the proper terminal zone response. The parameters - viscosity, two times, and two exponents - are less coupled than those in the HN equation. Each exponent is associated with a different relaxation time, and the two times in our model separate the terminal, crossover, and power law regions of the mechanical spectrum. The new model is better able to describe the rheology of commercial broad molar mass distribution polyolefins than the HN expression. We expect the ratio of the two relaxation times to correlate with polydispersity. We also discuss the limitations of using both the HN and our new model to interpret data sets of limited range.

Wednesday 6:00 Lubbock Memorial Civic Center

PO19

### **Melt rheology of poly(vinylidene fluoride): Evidence of long chain branching?**

Lauriane F. Scanu, Joseph M. DeSimone, George W. Roberts, and Saad A. Khan  
*Chemical Engineering, North Carolina State University, Raleigh, NC 27695*

Rheological measurements are used to study the influence of molecular weights and molecular weight distributions (MWD) on the melt polymer behavior of poly(vinylidene fluoride) (PVDF). These measurements are aimed at explaining the bimodal MWD displayed by PVDF when it is produced by continuous precipitation polymerization in supercritical CO<sub>2</sub> (scCO<sub>2</sub>). The rheological behavior of polymer melts is strongly influenced by their molecular weight and especially by their architecture and MWD. Commercial PVDF samples are used for comparison purposes and for testing the accuracy of empirical techniques on inferring structural information for PVDF. The rheological characterization of these samples reveals a different trend for one of them. Several rheological correlations are applied to the sample data and the presence of branching is identified in this sample. Monomodal and bimodal scCO<sub>2</sub>-polymerized PVDFs are rheologically characterized to infer their architecture and understand the bimodal MWD observed as the inlet monomer concentration is increased.

Wednesday 6:00 Lubbock Memorial Civic Center

PO20

### **Molecular weight dependence of fragility in polystyrene and poly(vinylpyridine)**

Patrick G. Santangelo, Riccardo Casalini, G C. Robertson, and C M. Roland  
*US Naval Research Laboratory, Washington, D.C. 20375*

The temperature dependence of properties in the vicinity of the glass transition is invariably non-Arrhenius, with the steepness of a T<sub>g</sub>-normalized plot ('fragility curve') often used to classify relaxation behavior. Such an approach has led to progress in revealing the effect of molecular architecture on the relaxation properties of polymers. For example, polymers possessing flexible, non-polar chain structures, without substantial pendant groups, exhibit narrow relaxation dispersions and weak temperature dependencies, while broad relaxation functions and segmental relaxation times which are more sensitive to temperature are generally associated with polymers whose structure engender more cooperative motion. We present mechanical spectra for a series of polystyrenes (PS), poly(2-vinyl pyridine)s (2VP) and poly(4-vinyl pyridine)s (4VP) of varying molecular weight. With the polymers possessing a similar backbone structure, the effect of pendant groups and chain ends on the segmental relaxation behavior is examined.

Wednesday 6:00 Lubbock Memorial Civic Center

PO21

### **Are we in equilibrium yet, Charlie Brown?**

Qingxiu Li<sup>1</sup>, Donald J. Plazek<sup>2</sup>, and Sindee L. Simon<sup>1</sup>

<sup>1</sup>*Chemical Engineering, Texas Tech University, Lubbock, TX 79409;* <sup>2</sup>*Dept. of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA 15261*

Glasses are inherently nonequilibrium materials, and consequently, their properties evolve toward equilibrium in a process known as structural recovery or physical aging. Recently, several authors have suggested that the equilibrium state is not reached even though properties have ceased to evolve. In this work, we present measurements of the enthalpy recovery of polystyrene (PS) at 90°C for aging times up to several months. In

addition, we analyze data in the literature to determine whether volume and enthalpy recovery cease prior to the material reaching its equilibrium density or enthalpy. Our results and others in the literature based on extrapolation of the liquid line suggest that, in fact, equilibrium is reached at temperatures below  $T_g$  when properties cease evolving.

Wednesday 6:00 Lubbock Memorial Civic Center PO22

### **Interfacial dynamics spectral boundary element algorithm**

Jingtao Wang, Yechun Wang, and Panagiotis Dimitrakopoulos

*Department of Chemical Engineering, University of Maryland, College Park, MD 20742-2111*

This talk describes a novel two- and three-dimensional Spectral Boundary Element algorithm for interfacial dynamics in Stokes flow. The main attraction of this approach is that it exploits all the benefits of the spectral methods (i.e. exponential convergence and numerical stability) with the versatility of the finite element method (i.e. the ability to handle the most complicated geometries). It also exploits all the benefits of the boundary element techniques, i.e. reduction of the problem dimensionality and great parallel scalability. Our algorithm is a high-order/high-accuracy methodology for the problem of droplet deformation in viscous flows. By applying this algorithm to several interfacial problems in extensional and shear flows, we find that our results are in excellent agreement with experimental findings, analytical predictions and previous numerical computations. Results for subcritical and supercritical capillary numbers will be presented.

Wednesday 6:00 Lubbock Memorial Civic Center PO23

### **Micro-macro simulation with anisotropic FENE dumbbell model**

Sunjin Song<sup>1</sup>, Ju M. Kim<sup>2</sup>, Kyung H. Ahn<sup>1</sup>, and Seung J. Lee<sup>1</sup>

<sup>1</sup>*School of Chemical Engineering, Seoul National University, Seoul 151-744, Republic of Korea;* <sup>2</sup>*Applied Rheology Center, Korea University, Seoul, Republic of Korea*

We will present the simulation results of micro-channel flow of FENE dumbbells including wall interaction using the Brownian Configuration Field method. As the interaction between FENE dumbbell and the wall is important in micro-channel flow, we included anisotropic drag and anisotropic Brownian force in the governing equation near the wall. For accurate and stable results, we used adaptive semi-implicit predictor-corrector method and DEVSS-G/DG scheme. The Couette flow was simulated first as a verification of our code, and we described the stretching and orientation of dumbbells with some parameter studies.

From the simulation result, we can observe that most of dumbbells align to about  $10^\circ$  to the flow direction, but some undergo clockwise tumbling due to Brownian motion. When the anisotropic drag and the anisotropic Brownian force is applied, the dumbbells are aligned to the flow direction with smaller angle and stretched more strongly, before showing lower steady stretch value than in the case of the isotropic drag and Brownian force. Solvent viscosity ratio affect not to orientation, but stretching, and the higher shear rate makes the dumbbells more aligned to the flow direction. And the stiffer dumbbells are less stretched and aligned to larger angle to the flow direction.

Wednesday 6:00 Lubbock Memorial Civic Center PO24

### **Modeling fiber spinning of PLA**

William Kohler, Anthony J. McHugh, and Prashant Shrikhande

*Chemical Engineering, Lehigh University, Bethlehem, PA 18015*

A modified version of a model for fiber spinning has been developed for Poly (lactic acid) (PLA). Comparisons are made to melt spinning data of Takasaki and coworkers for high L- content PLA (PLLA) and racemic mixtures of the L- and D- forms over a range of spin speeds from high to low speed conditions. The characteristic necking and "freeze off" under high speed conditions is not as severe with PLA as that observed in the earlier model systems, most likely due to the more highly entangled nature of PLA. To address this, the extended Pom-Pom model (XPP) is utilized to model the melt phase. Because of the stereochemistry of PLA, mixtures of the L- and D- forms result in an additional stereo-crystal formation with a higher melting temperature than the normal alpha-crystal formation. In addition to accurately capturing fiber diameter profiles for the PLLA, all the important features of spinning of the racemic mixture (r-PLA) are also successfully captured with our model. Besides diameter predictions, the model also successfully predicts the elongation to break of the spun fiber by correlating it to the calculated ratio of amorphous to total stress at the "freeze off" point. In modeling both PLLA and r-PLA, further insight is gained into

the relationship between thermally induced crystallization and flow-enhanced crystallization. In addition, results from the single- and multi-mode XPP model are compared.

Wednesday 6:00 Lubbock Memorial Civic Center

PO25

### **Modeling the blown film process**

Lars K. Henriksen<sup>1</sup> and Anthony J. McHugh<sup>2</sup>

<sup>1</sup>*Chemical and Biomolecular Engineering, University of Illinois, Urbana, IL;* <sup>2</sup>*Chemical Engineering, Lehigh University, Bethlehem, PA 18015*

Predictions for the blown film extrusion of low- and linear low-density polyethylenes (LDPE and LLDPE) are presented based on a modified version of our earlier two-phase model. The current algorithm includes the semi-crystalline rigid rod phase from the beginning of the simulation at the extrusion die exit. This approach removes the artificial switch point built into the previous model version, thereby eliminating the underlying discontinuities and resulting in a more robust model. This improved model is capable of fitting LLDPE and LDPE data over a broader range of BUR and  $f^*P$  while using only one set of fitting parameters per material. Model data fits of bubble radius, temperature, and crystallinity are shown for each material. The radius and temperature predictions are excellent, while the crystallinity predictions are the least accurate, although still reasonable approximations of the experimental data.

Wednesday 6:00 Lubbock Memorial Civic Center

PO26

### **Real-time access to experiment and theory in the rheology class room**

H. Henning Winter<sup>1</sup> and Marian Mours<sup>2</sup>

<sup>1</sup>*Chemical Engineering and Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003;* <sup>2</sup>*weisenheim am sand, Germany*

In spite of the significance that rheology has in technical applications, its full use is still limited to a small group of highly trained scientists and engineers. A wider appreciation can be gained by providing easier access to rheology, for instance, through an easy-to-use teaching software that can invoke rheological theory and experiments in the class room (and in the laboratory). An international collaboration was initiated with the objective of writing such software. We envision that students bring their laptop to class and, jointly with the teacher, analyze experimental data, perform calculations with published theory, view animation, and freely exchange rheological data and predictions from theory. Patterns may be found in the data and theories may be validated. Through the IRIS software, many of these features are already implemented and put to use in over 40 academic and industrial laboratories. Rheology will advance by the development of user-friendly methods as discussed here. In-depth data analysis and evaluation of theory will become easy enough to be performed after a few days of training. The new teaching methods will express rheology in its full complexity and, potentially, generate broad access to rheological concepts.

Wednesday 6:00 Lubbock Memorial Civic Center

PO27

### **Dynamic Monte Carlo simulation of polymer shear flow**

Saeed Al-Hassan and John R. Dorgan

*Chemical Engineering Department, Colorado School of Mines, Golden, CO 80401*

The use of on-lattice Monte Carlo simulation to predict melt rheological properties of polymers is explored. The methodology employed consists of the cooperative motion algorithm of Pakula and a derived biasing technique based on previous studies of Binder and Baushnagel. Chain correlation functions demonstrate that Rousian dynamics are obtained. The biasing technique is derived to be suitable for the face centered cubic lattice used in the simulations. In shear flow, a uniform linear velocity profile is obtainable for low molecular weight chains for all values of the biasing parameter. However, for larger chain lengths the velocity profile becomes distorted; this distortion is eliminated if the value of the biasing parameter is reduced. Use of the Kramers form for entropic springs allows the calculation of stress in the simulation providing a means for exploring rheological properties including viscosity and normal stress differences. Results are in excellent agreement with well-established experimental facts; a shear thinning viscosity is obtained, the first normal stress difference increases with shear rate, and the first normal stress coefficient decreases with shear rate. An alternative method of calculating the stress based on an analog to the stress-optical rule based on bond correlations is also examined.

Wednesday 6:00 Lubbock Memorial Civic Center

PO28

**Modeling aerosol transport in the vicinity of urban vegetative canopies**

Jeremy W. Leggoe, Elliott D. Eastep, Jessica N. Rendon, and Jason L. Williams

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In the urban environment, vegetative canopies usually do not extend beyond the adjustment region associated with the canopy leading edge. For isolated individual canopies, a large portion of the mean flow passes through the canopy, and the near-canopy wake is substantially altered in dimension and character compared to that expected for solid obstacles. The flow field associated with typical trees must therefore be regarded as substantially different to that associated with solid objects, and caution must be exercised in modeling trees as solid obstacles in urban canopy parameterizations. Models representing finite multi-tree forest stands were formulated to investigate the effect of tree spacing and arrangement on the canopy flow field. The velocity profiles for random and staggered 20% ground coverage arrays are virtually identical, indicating that a staggered array provides a reasonable approximation to a random arrangement. The flow field within random stands tended towards the behavior of a "block" canopy with increasing ground coverage. For 30% ground coverage and higher, it appears reasonable to model stands as homogeneous canopies, though the porosity of the "equivalent" homogenous canopy should be increased to account for the open space within the canopy. Implementation of the Sanz canopy turbulence model strongly influenced the flow and turbulence fields around finite canopies. Dissipation within the leading edge appears to strongly influence the local TKE field, eliminating the expected region of elevated TKE near the separation point. Peak TKE levels are instead observed downstream of the canopy, in the mixing region above the near-canopy wake zone. The velocity magnitudes at the lower levels of the canopy are not significantly affected by the implementation of the Sanz model, and neither are the velocities well above the canopy. Near the canopy top, however, significant differences in the velocity profiles arise.

Wednesday 6:00 Lubbock Memorial Civic Center

PO29

**HAAKE MARS - a new dimension in modularity**

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The new rheometer HAAKE MARS (Modular Advanced Rheometer System) shows a new level of modularity with interchangeable temperature control units, which cover a temperature range from -150 to 600 °C, a wide range of measuring geometries and interchangeable measuring heads and electronics. On top of that, special measuring equipment like an optical module for the simultaneous analysis of rheological properties and the microscopic structure of a sample is available, which in total gives a new dimension to the concept of "modularity" and flexibility. The rheometer's stand with unique design is characterized by an optimized force balance, in which active forces from the sample and reactive forces are in one plane, a lift with a high accuracy positioning system and a huge usable space for individual applications or to adapt modules for combined measurement methods, e.g. rheology and optical testing. The functions of the HAAKE MARS cover all rheological measurements in CR (controlled rate), CS (controlled stress) and CD (controlled deformation) mode, in rotation and oscillation, as well as normal force measurements including negative normal stresses, allowing the rheometer to perform tensile tests with and without axial movement. The built-in Ethernet interface allows high-speed data transfer up to 0,5 kHz as well as remote supervision and remote diagnostics. The HAAKE MARS platform will be introduced together with experimental results from selected materials.



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BS7, 15	GP6, 9	MS19, 65	PO29, 91	SC13, 35
BS8, 16	GP7, 9	MS20, 65		SC14, 35
BS9, 16	GP8, 10	MS21, 65	RM1, 33	SC15, 36
BS10, 16	GP9, 10	MS22, 66	RM2, 33	SC16, 36
BS11, 17	GP10, 10	MS23, 66	RM3, 33	SC17, 36
BS12, 17	GP11, 11	MS24, 66	RM4, 45	SC18, 47
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DS1, 3	GP14, 23	MS27, 77	RM7, 46	SC21, 48
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DS4, 4	GP17, 24	MS30, 78	RM10, 55	SC24, 58
DS5, 4	GP18, 24	MS31, 79	RM11, 56	SC25, 58
DS6, 12	GP19, 31	MS32, 79	RM12, 56	SC26, 59
DS7, 12	GP20, 31	MS33, 80	RM13, 56	SC27, 59
DS8, 13	GP21, 32	MS34, 80	RM14, 56	SC28, 60
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EM2, 27	MF2, 7	PL3, 45	SA1, 39	SC32, 72
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EM4, 28	MF4, 8	PO1, 81	SA3, 40	SC34, 73
EM5, 28	MF5, 8	PO2, 81	SA4, 40	SC36, 73
EM6, 37	MF6, 18	PO3, 82	SA5, 49	SC37, 74
EM7, 37	MF7, 19	PO4, 82	SA6, 49	
EM8, 38	MF8, 19	PO5, 82	SA7, 50	
EM9, 38	MF9, 20	PO6, 83	SA8, 50	
EM10, 74	MF10, 20	PO7, 83	SA9, 50	
EM11, 75	MF11, 20	PO8, 84	SA10, 61	
EM12, 75	MF12, 21	PO9, 84	SA11, 62	
EM13, 75	MF13, 21	PO10, 84	SA12, 62	
EM14, 76		PO11, 85	SA13, 62	
EM15, 76	MS1, 28	PO12, 85	SA14, 63	
EM16, 76	MS2, 29	PO13, 86	SA15, 63	
EM17, 77	MS3, 29	PO14, 86	SA16, 64	
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FI2, 69	MS6, 41	PO17, 87		SC2, 14
FI3, 69	MS7, 41	PO18, 87		SC3, 14
FI4, 70	MS8, 42	PO19, 88		SC4, 14
FI5, 70	MS10, 42	PO20, 88		SC5, 25
FI6, 71	MS11, 42	PO21, 88		SC6, 25
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# Plenary Lectures

8:30 AM Theater

**Monday, February 14**

**Stretched to breaking point: Measuring the transient extensional rheometry of complex fluids from the dilute solution to the melt**

Gareth H. McKinley

*Department of Mechanical Engineering, Massachusetts Institute of Technology*

**Tuesday, February 15**

*Bingham Lecture*

**Rheometry: From concentric cylinders to optical tweezers**

Christopher W. Macosko

*Department of Chemical Engineering and Materials Science, University of Minnesota*

**Wednesday, February 16**

**Rheology and microrheology of composite actin networks**

David Weitz

*Harvard University*

# Social Program

**Sunday, February 13**

**Welcoming Reception**

7:00 PM – 9:00 PM Atrium of the Holiday Inn and Towers

**Monday, February 14**

**Society Luncheon**

12:00 – 1:40 PM Lubbock Memorial Civic Center

Prof. David Boger, Laureate Professor at *University of Melbourne*, will give a talk titled “**Rheology and the Triple Bottom Line**”.

**Society Reception**

6:15 PM – 10:00 PM Caprock Winery

Busses will leave for the winery from the Holiday Inn at 6:15 PM.

**Tuesday, February 15**

**Business Meeting**

5:40 PM Room 107, Lubbock Mem. Civic Center

**Awards Reception**

7:00 PM – 8:00 PM Museum of Texas Tech

Busses will leave for the museum from the Holiday Inn at 6:45 PM.

**Awards Banquet**

8:00 PM – 10:00 PM Museum of Texas Tech

**Wednesday, February 16**

**Poster Session Refreshments**

6:00 PM – 8:00 PM Lubbock Memorial Civic Center