THE SOCIETY OF RHEOLOGY

75TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Sheraton Station Square Hotel
Pittsburgh, Pennsylvania
October 12-16, 2003

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Meeting Schedule

Monday, October 13, 2003

8:30	R. B. Bird (PL1)			
9:20	Coffee			
9:45	SM1	VF1	RS1	MM1
10:10	SM2	VF2	RS2	MM2
10:35	SM3	VF3	RS3	MM3
11:00	SM4	VF4	RS4	MM4
11:25	SM5	VF5	RS5	MM5
11:50	Lunch			
1:30	SM6	VF6	RS6	MM6
1:55	SM7	VF7	RS7	MM7
2:20	SM8	VF8	RS8	MM8
2:45	SM9	VF9	RS9	MM9
3:10	Coffee			
3:35	SM10	VF10	RS10	MM10
4:00	SM11	VF11	RS11	MM11
4:25	SM12	VF12	RS12	MM12
4:50	SM13	VF13	RS13	MM13
5:15	SM14	VF14	RS14	MM14
5:40	End			
7:00	Awards Reception			
8:00	Awards Banquet			

Tuesday, October 14, 2003

8:30	G. Marrucci (PL2)			
9:20	Coffee			
9:45	SM15	VF15	EA1	MM15
10:10	SM16	VF16	EA2	MM16
10:35	SM17	VF17	EA3	MM17
11:00	SM18	VF18	EA4	MM18
11:25	SM19	VF19	EA5	MM19
11:50	Lunch			
1:30	SM20	VF20	EA6	MM20
1:55	SM21	VF21	EA7	MM21
2:20	SM22	VF22	EA8	MM22
2:45	SM23	VF23	EA9	MM23
3:10	Coffee			
3:35	SM24	VF24	EA10	LC1
4:00	SM25	VF25	EA11	LC2
4:25	SM26	VF26	EA12	LC3
4:50	SM27	VF27	EA13	LC4
5:15	End			
5:30	Business Meeting			
7:00	Tuesday Night Reception			

Wednesday, October 15, 2003

8:30	A. B. Metzner (PL3)			
9:20	Coffee			
9:45	SM28	VF28	EA14	LC5
10:10	SM29	VF29	EA15	LC6
10:35	SM30	VF30	EA16	LC7
11:00	SM31	VF31	EA17	LC8
11:25	SM32	VF32	EA18	LC9
11:50	Lunch			
1:30	SM33	BR1	EA19	LC10
1:55	SM34	BR2	EA20	LC11
2:20	SM35	BR3	EA21	LC12
2:45	SM36	BR4	EA22	LC13
3:10	Coffee			
3:35	SM37	BR5	EA23	LC14
4:00	SM38	BR6	EA24	LC15
4:25	SM39	BR7	EA25	LC16
4:50	SM40	BR8	EA26	LC17
5:15	SM41	BR9	EA27	LC18
5:40	End			
6:00	Poster Session & Refreshments			

Thursday, October 16, 2003

8:05	SM42	BR10	ER1	LC19
8:30	SM43	BR11	ER2	LC20
8:55	SM44	BR12	ER3	LC21
9:20	SM45	BR13	ER4	LC22
9:45	Coffee			
10:10	SM46	BR14	ER5	LC23
10:35	SM47	BR15	ER6	LC24
11:00	SM48	BR16	ER7	LC25
11:25	SM49	BR17	ER8	LC26
11:50	SM50	BR18	ER9	LC27
12:15	End			

Session Codes

BR = Biorheology
EA = Entangled Polymers and Analytical Rheology
ER = Extensional Rheology
LC = Liquid Crystalline Polymers and Self-Assembling Fluids
MM = Microrheology, Microfluids and MEMS
PL = Plenary Lectures
RS = Rheology of Solids and Near-Solids
SM = Suspension and Multiphase Fluids
VF = Viscoelastic Flows and Instabilities

Contents

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Grand Station I/II PL1

Dumbbells, trumbbells, shishkebabs, and pearl necklaces — a gallimaufry of results

R. Byron Bird
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The history of the molecular theory of rheology for the last seventy-five years will be reviewed, from the point of view of the applications of the theory. The presentation will not be mathematical, but will be concerned with the bead-spring-rod mechanical models of polymer molecules and the types of flows for which useful results can be obtained.

Among the applications, we will discuss are: the development of constitutive equations, the development of combining laws for mixtures, the deduction of the macromolecular motions, the molecular weight dependence of various properties, the relation between molecular architecture and physical properties, the search for relations among various properties, the prediction of rheological phenomena, and the elucidation of nonisothermal phenomena.

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Monday 9:45 Grand Station I SM1

Effect of film formation on tack of waterborne adhesives

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[1]Chemical Engineering, Princeton University, Princeton, NJ; [2]Adhesives Division, National Starch and Chemical Company, Bridgewater, NJ

Waterborne adhesives are aqueous colloidal dispersions of soft polymer particles (T_g~0 °C) typically having an average size of 1 to 2 μm. When a thin film of WBA is squeezed between a pair of porous substrates, the hydrodynamic lubrication flow in the gap is accompanied by imbibition of water into the substrates (particles do not imbibe if they are larger than the pore size). The latter causes the particle concentration to increase to maximum packing, triggering particle coalescence and formation of a rigid polymer film that binds the substrates together. The strength of the adhesive bond is then determined by the force/work required to separate the substrates. We investigate, through a combination of theory and experiments, the effect of imbibition, particle coalescence, and adhesive rheology on the force required to squeeze/separate porous substrate.

Monday 10:10 Grand Station I SM2

Soft colloid-polymer mixtures: Kinetic transitions and osmotic interactions

Emmanuel Stiakakis[1], George Petekidis[1], Dimitris Vlassopoulos[1], and Jacques Roovers[2]
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We use well-defined colloidal star polymers exhibiting ultrasoft repulsions, in order to explore glass formation and melting phenomena. In particular, we consider mixtures of such colloids with linear homopolymer chains consisting of the same monomers, in solvents of intermediate quality, where temperature can serve as a means to increase the effective star volume fraction. With the aid of shear rheometry and dynamic light scattering we demonstrate that if the linear chain molecular weight is much smaller than the star arm molecular weight, penetration is favored, and the stars swell, yielding soft glasses. On the other hand, if the linear chain molecular weight exceeds that of the star arm, the mixture exhibits liquid-like behavior (melting) under the influence of osmotic pressure effects. The latter are manifested first as star shrinkage and then as star depletion. Further, we construct kinetic phase diagrams, which are discussed in terms of jamming transitions. These results offer new possibilities for the molecular control of the flow properties of soft colloids.

Monday 10:35 Grand Station I SM3

Shear thickening of attractive particles in suspensions and gels

Vijay Gopalakrishnan and Charles F. Zukoski
Chemical and Biomolecular Engineering, University of Illinois at Urbana Champaign, Urbana, IL 61801

Suspension flow properties play a vital role in product quality in the paints, coatings and other similar industries. Some concentrated colloidal suspensions, at high shear stresses display shear thickening. The stress demarcating the transition from shear thinning to shear thickening regimes is called the critical stress. Previous experiments on hard sphere-like systems and hard spheres with repulsions demonstrate that shear thickening is the result of stress driven "hydroclusters" which trap solvent between the particles thereby causing an increase in the lubrication stresses. These experiments and simulations have concluded that hydroclusters are the result of a force balance between shear and Brownian stresses. Our investigation looks at thickening in suspensions of attractive particles. The strength of the interparticle attraction is altered by depletion interactions between hard spheres. The strength of attraction is set by increasing the concentration of non-adsorbing polymer while the polymer radius of gyration sets the range. Owing to the resulting attractions, particles in these suspensions have a general tendency to cluster thereby suggesting that shear thickening should commence at lower stresses. However, our observations indicate the very opposite. Our experiments investigate colloid volume fractions from 0.45 to 0.49 with a ratio of polymer radius of gyration to the particle radius of 0.053, looking at the progression from hard spheres to polymer concentrations deep into the gel phase. It has been suggested that both gelation and thickening have been associated with jamming and our observations suggest a difference- gelled systems shear thicken and the thickening seems to be a smooth progression from the ungelled suspensions. Present scaling models do not capture the observed trend for attractive systems. We discuss changes to currently accepted models and provide conclusions consistent with that of past experiments and simulations.

Monday 11:00 Grand Station I SM4

Shear induced anisotropy in reversibly aggregated suspensions

Hans Hoekstra[1], Jan Vermant[1], Jan Mewis[1], and Theyencheri Narayanan[2]
[1]Department of Chemical Engineering, K.U.Leuven, Leuven, Belgium; [2]ESRF, Grenoble, France

The flow-induced structure of a thermo-reversibly aggregated colloidal suspension has been studied over the full range of relevant length scales, in-situ and time resolved. It recently has been demonstrated that shear flow induces anisotropy in the microstructure of these materials at large length scales [1]. For the 2 dimensional case the anisotropy has been linked to a directional dependence of aggregation and breakup [2]. A direct consequence of this mechanism is that the anisotropy in the microstructure should persist to the smallest length scales in the sample.

In the present study 27 nm octadecanol coated silica particles, dispersed in n-tetradecane, were used as a model system. This system forms a thermo-reversible gel that shows distinct anisotropic light scattering patterns when subjected to shear flow. To characterize the microstructure on small length scales, SAXS measurements were conducted at the European Synchrotron Radiation Facility. The analysis of Wagner and Ackerson [3], using decomposition of the structure factor with help of spherical harmonics, was employed to detect anisotropy in these patterns. As in the case of light scattering, a pronounced anisotropy is observed. When the gels were strongly undercooled no anisotropy was observed in shear flow. To bridge the gap in length scales that exist between SALS and SAXS also USAXS measurements were conducted during flow. Based on the combined SALS-SAXS-USAXS measurements we conclude that the anisotropy in the microstructure of weakly aggregated suspensions in shear flow persists to very small length scales, as was observed in the two dimensional counterparts.

The relevance of the structural anisotropy and the pertinent length scale for the rheological behaviour will be discussed.

[1] Varadan P, Solomon MJ, Langmuir **2001**, 17, 2918. [2] Hoekstra H, Vermant J, Mewis J, Fuller GG, submitted to Langmuir **2003**. [3] Wagner NJ, Ackerson BJ, J. Chem. Phys. **1992**, 97, 1473.

Monday 11:25 Grand Station I SM5

The rheology of model polyampholyte stabilized colloidal dispersions: Comparison of experiments and theory

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The adsorption of polyampholytes on colloidal surfaces provides a mechanism for control of stability, phase behavior, and rheology that is of use in numerous technologies, such as pharmaceuticals and the photographic industries. However, the interparticle interactions that arise from electrostatic, polymer steric, and depletion forces are strongly coupled. In this work we propose a simplified, yet robust for model for the interparticle interactions arising from adsorbed polyampholytes. The model is based on the osmotic overlap interaction potential where the osmotic pressure in the adsorbed polymer brush is related to the bulk osmotic pressure of the polyampholyte in solution. Experimental results are presented for the rheology, phase behavior, and colloidal microstructure for a model dispersion of 30nm silica particles in a buffered, aqueous gelatin solution over a range of particle, gelatin and electrolyte concentrations and for varying pH. The model potential is verified by small angle neutron scattering measurements of the colloidal microstructure. Quantitative predictions for the suspension viscosity are demonstrated. Further, the proposed model is demonstrated to provide a master curve for the low shear viscosity of numerous data sets on similar systems published in the literature.

Symposium VF
Viscoelastic Flows and Instabilities

Organizers: Jonathan Rothstein and Bamin Khomami

Monday 9:45 Grand Station III VF1

Monte Carlo simulation of uniaxial extension of dilute polymer solutions

Xianfeng Li[1] and Morton M. Denn[2]
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An efficient Monte Carlo method using the Bond Fluctuation Model was used to simulate uniaxial extension of dilute polymer solutions. The longest relaxation times and diffusion coefficients show the expected Rouse-like behavior, and the calculated extensional viscosity is linear in chain length. The Monte Carlo simulations agree with published experiments and Brownian dynamics simulations for DNA molecules. “Molecular individualism” is observed in the unraveling of the polymer chain.

Monday 10:10 Grand Station III VF2

Self-consistent Brownian dynamics simulation of rheology of polymer blends

Venkat Ganesan, Victor Pryamitsyn, and Bharadwaj Narayanan
Chemical Engineering, Univ. of Texas at Austin, Austin, TX 78712

We outline a novel methodology which combines “on-the-fly” the self-consistent field theory for inhomogeneous polymeric systems with a Brownian Dynamics algorithm. Such a procedure allows one to capture viscoelastic effects within the framework of a coarse-grained simulation approach. We showcase our results in the contexts of equilibrium and dynamical effects in polymer blends. We consider both symmetric (in terms of molecular mass and mobilities) as well as asymmetric polymer blends. Our results are mainly focused on the interplay between the thermodynamical transitions and the rheology of polymer blends. Specifically, we focus on the shear induced shifts in phase transitions, the transitions from weakly inhomogeneous to strongly inhomogeneous rheology, slip phenomena in polymer blends etc.

Monday 10:35 Grand Station III VF3

Brownian dynamics simulations with hydrodynamic interaction for polystyrene solutions in extensional and shear flow

Chih-Chen Hsieh and Ronald G. Larson
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We have developed a method to include full hydrodynamic interaction (HI) using the Rotne-Prager tensor into the bead-spring model for Brownian dynamics simulations of the transient nonlinear rheological properties of dilute polymer solutions. The hydrodynamic interaction parameter h^* is obtained a priori by matching the drag force from a fully extended bead-spring model with that from Batchelor's theory for cylindrical rods. This procedure gives a value of h^* that decreases as N, the number of beads, increases. We performed the simulations for dilute polystyrene solutions in extensional flow with molecular weights 1.95, 3.9 and 10.2 million. The agreement between experimental data and simulation results for the transient Trouton ratio vs. strain is very good from low to medium strains. However, the plateaus at high strains predicted by the simulations were higher than measured. We also found that hydrodynamic interaction hinders the unraveling of a polymer chain in strong extensional flow ($Wi >> 1$) due to the hydrodynamic clustering of beads. In steady shear flow, the combination of hydrodynamic interaction and finite spring extensibility resulted in a shear-thinning-thickening-thinning behavior with the increase of shear rate. The simulated first normal stress coefficient does not match the experimental results quantitatively due to an insufficient number of beads (no more than 80) to represent the hydrodynamic interactions accurately enough to bring the value of h^* down to 0.25, a value attained only when > 300 beads are used. A negative second normal stress coefficient is also predicted, which differs in sign for the value obtained in earlier work using consistent-averaging.

Monday 11:00 Grand Station III VF4

Effects of spring connector force laws on viscosity and macromolecular extension in steady shear flow of dilute solutions of bead-and-spring polymer chains

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For free-draining polymer chains, bead-and-spring models employing either nonlinear springs or internal viscosity have been shown to predict non-Newtonian viscosity, whereas the viscosity predicted for free draining chains of Hookean springs (Rouse model) is Newtonian. However, the behavior of these spring connector models in non-draining chains with excluded volume has not been established. Dissipative Particle Dynamics (DPD) simulations of chains of Hookean and FENE springs, both with and without internal viscosity, have been conducted to examine the dynamical behavior of these chain models in the presence of hydrodynamic interaction and excluded volume. All chain models, including the Hookean spring chain without internal viscosity, exhibit shear-thinning intrinsic viscosity curves. Surprisingly, the intrinsic viscosity curves are nearly identical for all the models tested, indicating little influence of spring connector type or internal viscosity on shear-thinning of viscosity. Similar behavior is observed for the normal stresses. Spring connector force type, but not internal viscosity, is found to have a strong influence on predicted macromolecular extension ratios, however. Hookean spring chains exhibit greater extensions than comparable FENE spring chains at equivalent shear rates.

Monday 11:25 Grand Station III VF5

Cost-effective, multi-mode FENE bead-spring models for dilute polymer solutions

Rayhaneh Akhavan, Qiang Zhou, and Jin Liu
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Multi-mode Finitely Extensible Nonlinear Elastic (FENE) bead-spring models, FENE-M and FENE-MR are presented as cost-effective alternatives to the FENE chain. The cornerstone of the new models is an approximate form of the Warner spring force law which remains invariant under the transformation to normal coordinates. This allows the governing equations to be solved in normal coordinates, where different modes are decoupled. Utilizing this decoupling, FENE-M replicates the dynamics of a FENE chain in general flow kinematics at a cost which is O(1/N2) times the most efficient semi-implicit numerical solution of a FENE chain or O((N+1)/3) times that for a FENE dumbbell, where N denotes the number of beads in the chain. A reduced form of this model, referred to as FENE-MR, is also proposed, in which the cumulative behavior of modes 2 through (N-1) is captured in a single representative mode. FENE-MR replicates the stresses predicted by a FENE chain in general flow kinematics at a cost only 35% higher than a FENE dumbbell. The formulation of FENE-M and FENE-MR models can also be applied to closure approximations. Here, we apply these concepts to the FENE-LS dumbbell closure to develop the FENE-LSM and FENE-LSMR chain closures. FENE-LSMR closely approximates the FENE chain dynamics at a cost only twice that of a FENE-P dumbbell. The proposed FENE-LSMR and FENE-MR models have been implemented in DNS and in micro-macro simulations using a Backward-tracking Lagrangian Particle to study the physics of drag reduction by dilute polymer solutions in a turbulent channel flow. The computations reproduce many of the flow features observed experimentally, including the condition of zero Reynolds shear stress at MDR (70% DR). In addition, the computations show that MDR is not a unique state.

Symposium RS
Rheology of Solids and Near-Solids

Organizers: Greg McKenna and Tony McHugh

Monday 9:45 Grand Station IV RS1

Elastic instabilities in rubber: Aneurysms, wrinkles and knots

Alan N. Gent
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Various types of instability in a neo-Hookean elastic solid are reviewed: the expansion of small cavities in rubber blocks when they are supersaturated with a dissolved gas or when the block itself is subjected to a critical dilatant stress (negative pressure), surface wrinkling caused by compression of a half-space parallel to the surface, and knots that appear on twisting a stretched rubber rod. Unrestrained growth of a cavity is predicted at a dilatant stress of 5E/6, where E is Young's modulus [1]. Internal voids appear suddenly when the dilatant stress approaches this value [2]. Failure often follows. The second instability is predicted to occur in the surface of a half-space at moderate compressive strains, between 33 and 55 % [3]. When an elastic block is bent, an instability would be expected at 44 % compression of the inner surface. Experimentally, sharp creases appear suddenly, but at only 35 % compression when bending is only about one-half as severe as predicted [4]. These creases might pass undetected in service although they are potential failure sites. When a stretched rubber rod is twisted, kinks or knots form suddenly at a critical amount of torsion, in good agreement with theoretical predictions [5].

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2. A. N. Gent, Rubb.Chem. Technol. 63, G49-G53 (1990).
3. M. A. Biot, "Mechanics of Incremental Deformations", Wiley, New York, 1965.
4. A. N. Gent and I.-S. Cho, Rubb.Chem. Technol. 72, 253 (1999).
5. A. N. Gent and K.-C. Hua, J. Non-Linear Mech., in press (2003).

Monday 10:10 Grand Station IV RS2

Rheo-dielectric behavior of poly(ethylene oxide) containing lithium perchlorate

Yumi Matsumiya[1], Nitash P. Balsara[1], and Hiroshi Watanabe[2]
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For a low-M poly(ethylene oxide) (PEO; M = 1000) containing relatively concentrated lithium perchlorate (0.1 and/or 0.2 Li atom per EO monomer), dielectric measurements were conducted in a quiescent state as well as under steady shear. In the quiescent state, this PEO/Li system exhibited prominent dielectric dispersion attributable to the electrode polarization of Li cations. These cations were not freely moving in the matrix of PEO chains but were dynamically bound to the chains (at the oxygen in the monomer unit) to form a transient network of the chains, as suggested from a fact that the zero-shear viscosity of the PEO/Li system was orders of magnitude larger than the viscosity of neat PEO. Under fast steady shear, the electrode polarization was even more enhanced. This enhancement was attributable to shear induced release of the Li cations from the PEO chains and the resulting rupture of the transient (dynamic) network of these chains. Correspondingly, the system exhibited shear-thinning of its steady flow viscosity in a range of shear rate where the electrode polarization was enhanced. The magnitude of thinning was close to the magnitude of the enhancement of the electrode polarization (by a factor of 3). This result suggested that the thinning corresponds to an acceleration of the chain motion resulting from the release of the Li cations (that dynamically bind/crosslink the chains in the quiescent state).

Monday 10:35 Grand Station IV RS3

Normal-stress differences and the detection of disclinations in nematic elastomers

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A continuum model is used to investigate the radial expansion of a right circular cylindrical specimen composed of a nematic elastomer. Numerical solutions show that, above a certain radial expansion of the specimen, the material has a energetic preference for a biaxial state involving a disclination of strength +1 along the cylinder axis. Surrounding such a disclination is a core with radial dimension on the order of 10^{-2} μm, which coincides with observations of disclinations in conventional liquid-crystalline melts. Examination of the first normal stress-difference reveals a non-monotonic dependence on the extent of radial expansion and suggests a practical experimental method for testing the predictions of the model.

Monday 11:00 Grand Station IV RS4

Non-universality of elastic exponents in random bond-bending networks

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How does the shear modulus of a semiflexible network vanish that network is made progressively more sparse? To study that question, we numerically investigated the rigidity percolation transition in two--dimensional flexible, random rod networks with freely rotating cross-links. To study the elasticity of semiflexible networks near the rigidity percolation transition, we find it helpful to distinguish between the critical exponents controlling the fractal structure and diverging length scale of the percolating rigid cluster within the network and the elastic exponent which controls the vanishing of the static shear modulus at the transition. Near the transition, we find that the networks are dominated by bending modes and the elastic moduli vanish with an elastic exponent $f=3.0\pm0.2$, in contrast with central force models which share the same geometric exponents with our semiflexible, bond-bending model. This indicates that universality for geometric quantities does not imply universality of elastic properties near the transition.

Monday 11:25 Grand Station IV RS5

Stress and birefringence relaxation in end-linked elastomers with pendent chains

Ashish Batra[1], Mohend Chaouche[2], Claude Cohen[1], and Lynden A. Archer[1]
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We have performed simultaneous stress and birefringence relaxation studies on end-linked poly(dimethylsiloxane) networks with pendent chains as a function of molecular weight of pendent chains and cross-link density under uniaxial extension at strains within the linear viscoelastic regime. These networks are prepared by end-linking a mixture of low polydispersity difunctional vinyl terminated PDMS with approximately 10 wt % of low polydispersity monofunctional PDMS chains with a tetrafunctional cross-linker. The cross-link density can be controlled by the molecular weight of the precursor difunctional PDMS. The molecular weight of pendent chains is varied from 56k to 240k in two sets of networks with elastic chains of 7.5k and 17k. We find that the stress-optical rule holds not only at steady state, but also through out the relaxation time scale studied such that the normalized stress and birefringence relaxation curves overlap. This is in contrast to some recent results with polybutadiene networks that showed that birefringence relaxes faster than stress and changes sign during recovery from creep. The experimental relaxation curves fit the Chasset-Thirion equation quite well, and although the value of the exponent m is extremely sensitive to the values of the other fitted parameters (G_e and τ), it scales inversely with the molecular weight of the pendent chains for constant cross-link density networks

Symposium MM
Microrheology, Microfluids and MEMS

Organizers: Gerry Fuller and Kalman Migler

Monday 9:45 Grand Station V MM1

Geometrically mediated breakup of drops in microfluidic devices

Darren R. Link[1], Shelley L. Anna[2], David Weitz[1], and Howard A. Stone[2]
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Microfluidic technology offers capabilities for the precise handling of small fluid volumes. In particular, recent efforts have focused on microfluidic routes to manufacturing emulsions [1, 2]. The capability to achieve narrow distributions in drop sizes via such methods has also led to interest in using small droplets for templating and encapsulation, or as micro-mixers and chemical reactors. In this paper, we demonstrate two methods for passively controlling the size and size distribution of small droplets in microdevices fabricated with conventional soft lithography techniques. The microdevices take advantage of pressure-driven flow and geometrically simple configurations to break pre-formed emulsion droplets. The first configuration exploits the extensional flow in the neighborhood of the stagnation point at a T-shaped junction to split drops into either equal-sized or asymmetric droplets. We observe that increasingly higher flow rates are needed to achieve breakup as the initial drop size decreases, and we present an analytical model to understand the breaking to non-breaking transition in terms of stretching of drops in an extensional flow. While previous microfluidic routes to emulsification have not allowed simultaneous formation of very small droplets at high dispersed phase volume fractions, we show that sequential application of geometrically-mediated breakup at a T-junction facilitates the precise conversion of large initial slugs of the dispersed phase into small droplets comparable in size to the channel cross-section without altering the dispersed phase volume fraction. Finally, we explore an alternative passive breakup configuration which uses flow past isolated obstacles to break a predetermined fraction of the droplets.

[1] T. Thorsen, R.W. Roberts, F.H. Arnold, S.R. Quake, Phys. Rev. Lett. 86, 4163 (2001).
[2] S.L. Anna, N. Bontoux, H.A. Stone, Appl. Phys. Lett. 82, 364 (2003).

Monday 10:10 Grand Station V MM2

Microfluidic analogue of the 4-roll mill: Pressure-driven flow devices with adjustable flow type

Steven D. Hudson, Frederick R. Phelan, and Joao T. Cabral
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A unique pressure-driven microfluidic device with adjustable flow type is developed. The device contains a stagnation point, so that fluid properties can be studied at long material residence times in extensional, rotational, shear and mixed flows. Two- and three-dimensional Stokes-flow simulations are used to design channel dimensions and calculate flow type and strength in the stagnant region. The device is designed and constructed to optimize flow strength, enhance flow stability and permit rapid change of flow conditions. Drops in immiscible fluids are examined using a computer-controlled device with image analysis feedback. Single-drop deformation and relaxation and collision of drop pairs are demonstrated. Measurement of polymer chain orientation is also planned.

Monday 10:35 Grand Station V MM3

Velocity profiles in circular microchannels with hydrophobic and hydrophilic surfaces

Lucy E. Rodd[1], Shane T. Huntington[2], Katja Lyytikainen[3], David V. Boger[1], and Justin J. Cooper-White[1]
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In traditional macro-scale fluid dynamics problems for fully-developed Newtonian pipe flow, a single no-slip boundary condition is often used to describe the fluid-wall interactions. Such fluid-wall interactions may arise from surface hydrophobicity, surface charge, or roughness. However in micro-scale flows, high surface to volume ratios inherent to microchannels, amplify the importance of these surface-related forces. Depending on the surface character of microchannel surfaces, the bulk velocity profile may be modified significantly when compared with that predicted by classical fluid dynamics. Such surface-related phenomena have already been observed in the work of Tretheway and Meinhart [1], who observed a slip velocity in laminar Newtonian flow ($Re = 0.18$) over hydrophobic surfaces. Similar phenomena were also observed by Choi et al. [2].

This work investigates the fully developed velocity profiles of Newtonian liquids in cylindrical microchannels. The surfaces of 57 μm diameter glass capillaries have been treated to make them either hydrophobic or hydrophilic. The profiles resulting from each of these surface treatments have been quantified using a particle tracking velocimetry technique, using fluorescent laser-scanning confocal microscopy. 450 nanometre fluorescent tracer particles have been used to obtain velocity measurements to within < 1 micron of the wall.

[1] Tretheway, D.C. and C.D. Meinhart, *Apparent fluid slip at hydrophobic microchannel walls*. Physics of Fluids, 2002. **14**(3): p. L9-L12.
[2] Choi, C.-H., K.J.A. Westin, and K.S. Breuer, *Slip Flows in Hydrophilic and Hydrophobic Microchannels*. Physics of Fluids, 2003. **15**(10): p. 2897-2902.

Monday 11:00 Grand Station V MM4

Breakup of a fluid in a confined geometry

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We investigate the influence of geometrical confinement on the breakup of long fluid threads in the absence of imposed flow using a Lattice Boltzmann model. Our simulations primarily focus on the case of threads centered coaxially in a tube filled with another Newtonian fluid and subjected to both impulsive and random perturbations. We observe a slowing down of the rate of thread breakup ('kinetic stabilization') over a wide range of the confinement and find that the relative surface energies of the liquid components influence this effect. There is a transition in the late-stage morphology between spherical droplets and tube 'plugs' when the ratio of the tube radius to the initial thread radius (confinement ratio, L) is less than 2.3. Apart from changes in the rate of thread breakup, we find that this process is sensitive to the nature of the initial thread perturbation under high confinement conditions (i.e., when becomes L less than about 1.9). Impulsive perturbations led to a 'bulging' of the fluid near the tube wall, followed by thread breakup through the propagation of wave-like disturbances (‘end-pinch instability’) initiating from thread rupture points that ‘nucleate’ from the bulges. Random impulses along the thread, modeling thermal fluctuations, led to a complex breakup process involving a competition between the capillary wave and end-pinch instabilities. We also briefly compare our tube simulations to threads confined between parallel plates and to multiple interacting threads under confinement. Similarities between thread breakup in tube and parallel plate geometries are observed, although a greater extent of confinement is required to ‘stabilize’ thread breakup under parallel plate confinement. Strong collective motions involving adjacent threads characterize the multiple thread breakup process.

Monday 11:25 Grand Station V MM5

Oscillatory behavior and pattern formation in binary fluids flowing in patterned microchannels

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Through computer simulations, we probe the behavior of a binary fluid that consists of two immiscible components, A and B, which are driven by an imposed pressure gradient to flow through a chemically patterned, three-dimensional microchannel. The binary fluid is characterized by an order parameter, which represents the difference in the density of the A and B components. The evolution of the order parameter is described by a modified Cahn-Hillard equation with the advection term.

Two different arrangements of chemically distinct patches on the surfaces were investigated. In the first study, the top and bottom of the microchannel are decorated with a checkerboard pattern. Each checkerboard is composed of two A(B)-like patches, which are preferentially wetted by the A(B) fluid. The first B(A) patch is placed in the way of the A(B) stream. The most interesting behavior occurs near the sidewalls, where we observed the simultaneous periodic formation of A-in-B and B-in-A droplets. The system bifurcates between time-independent behavior and different types of non-decaying oscillations. We plot a bifurcation diagram that shows surprisingly complex behavior, including "memory" effects in the system.

In the second study, we consider just two patches-that is, one A and B patch--on the top and bottom substrates. In this case, morphological instabilities give rise to spatio-temporal periodic patterns in the center of channel. The observed structures may be regarded as traveling waves, which occur downstream of the patterned region. Namely, the fluid exhibits a dynamic "braiding" at low Reynolds number. We isolate conditions where this structure is similar to "slug" flow, which may be important in terms of microfluidic applications. In both examples, the morphological instabilities and surprisingly complex behavior is observed even in the absence of hydrodynamic interactions; the non-linearity is introduced through the interplay between the advection and the interactions with the patterned substrate.

Monday Afternoon

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Monday 1:30 Grand Station I SM6

Rheology and microrheology of microgels and compressed emulsions

Eugene Pashkovski[1], Luca Cipelletti[2], Suliana Manley[3], and David Weitz[3]
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Concentrated colloidal systems such as suspensions, emulsions, gels and pastes display complex and very intriguing behavior reflecting their metastability and structural disorder. Their rheological response depends on sample' age in a way that is similar to the responses of molecular and spin glasses to external perturbations. For these very different systems, the age-dependent relaxation time increases almost proportionally to the sample age. This suggests a general approach for studying aging phenomena in these soft colloidal glasses based on analysis of fluctuation-dissipation plots. We analyze the violation of Generalized Stokes-Einstein Relation (GSER) combining rheology and light scattering. We use creep and stress relaxation measurements in combination with low-angle dynamic light scattering and diffusing wave spectroscopy for xanthan pastes and water-in oil compressed emulsions. We present fluctuation-dissipation plots that show evolution of these systems during aging.

Monday 1:55 Grand Station I SM7

Structure in concentrated colloidal gels: Relation to interparticle potential and effect of shear flow

Stacey L. Elliott[1], Robert J. Butera[1], and Norman J. Wagner[2]
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Commercial coatings contain high concentrations of colloidal particles that are aggregated to some degree. The application latitude and final properties of the coating are profoundly influenced by the resulting microstructure. With the proper attractive interaction and volume fraction of particles, these dispersions will form a gel. Dynamic light scattering and linear viscoelastic measurements suggest that these colloidal gels exhibit behavior similar to that of irreversibly crosslinked polymer gels. Specifically, the shear moduli show a power law dependence on frequency and the autocorrelation function exhibits a power law decay as the gel structure evolves. Since this power law behavior is characteristic of the gel microstructure, we use power law exponents extracted from the oscillatory shear rheology and fiber-optic quasielastic light scattering to describe the relationship between the interparticle interactions and the aggregate structure in concentrated dispersions. We find that reducing the potential barrier in charged acrylic latex by adding sodium chloride increases the power law exponent, indicating a more open structure. Furthermore, a shear flow was applied to the gelled samples and the re-aggregation was monitored; a smaller power law exponent was observed, implying that the shear produced a more compact aggregate.

Monday 2:20 Grand Station I SM8

Yielding and rearrangements in colloidal glasses with varying interparticle interactions

George Petekidis[1], Florian Ozon[1], Dimitris Vlassopoulos[1], Matthias Ballauff[2], and Peter N. Pusey[3]
[1]Institute of Electronic Structure & Laser, FORTH, Heraklion, Crete 71110, Greece; [2]Universtity of Karlsruhe, Karlsruhe, Germany; [3]Unviversity of Edinburgh, Edinburgh, United Kingdom

We present a study of yielding and microscopic rearrangements in hard and soft sphere colloidal glasses by combining conventional rheology, Fourier Transform rheology and the technique of Light Scattering Echo. Creep and recovery measurements and dynamic strain sweeps, compensated by light scattering echo which measures the extent of irreversible particle rearrangement under oscillatory shear, show that the glasses of hard PMMA particles can tolerate surprisingly large strains, up to at least 15%, before yielding irreversibly. This behaviour was attributed to 'cage elasticity', the ability of a particle and its cage of neighbours to retain their identity under quite large distortion. In the lower concentration glasses we find that particle trajectories are partly reversible under strains which significantly exceed the yield strain. The onset of irreversible rearrangements measured by LS echo decreases with decreasing frequency revealing the interplay between shear and Brownian forces. Fourier transform rheology monitors the increase of higher harmonics in the stress signal when the system starts to yield. The effect of interparticle interactions is studied using soft thermoreversible migrogel particles where the interactions and the effective volume fraction may be tuned by temperature.

Monday 2:45 Grand Station I SM9

Structure and dynamics of hard fractal nanoparticle suspension

William E. Smith and Charles F. Zukoski
Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Fumed materials are used in a wide range of industrial applications. The low mass concentration needed to modify rheological properties is of great technological importance. The complexity of the surface chemistry of fumed silica produces challenges in separating the hydrodynamic and thermodynamic contributions. This study develops a model system and allows for the opportunity to study the thermodynamics and hydrodynamic characteristics of the suspension. Fumed silica is coated with 3-(trimethoxysilyl) propyl methacrylate and suspended in tetrahydrofurfuryl alcohol. The residual surface charge is neutralized using aqueous nitric acid and verified through electrophoresis, ultra small angle x-ray scattering, and viscosity measurements. The experiments and theories pertaining to suspension thermodynamics and mechanics of spheres suspended in a Newtonian medium experiencing volume exclusion interactions are used to study a suspension of fractal aggregates. The thermodynamics, microstructure, and rheology of the suspension are experimentally determined. These studies measure the intrinsic viscosity and characterize the viscosity as concentration of fumed silica increases, comparing the hydrodynamic and thermodynamic properties of the suspension. At sufficiently high concentrations, shear thickening is observed and these results are also compared with hard spheres.

Monday 3:35 Grand Station I SM10

Shear controlled aggregation and break-up in suspensions, studied with video microscopy

Michael H. Duits, Valentin A. Tolpekin, Dirk van den Ende, and Jorrit Mellema
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We used video microscopy to study the behavior of two kinds of aggregating suspensions in shear flow. 1) Concentrated suspensions of hard spheres with a bimodal size distribution provide a system with a very rich behavior. We performed an experimental study, focused at the effective pair potential between (sparse) large spheres, as caused by the presence of (much more abundant) small spheres. This potential is considered to contain an attractive well in the contact region, but also a repulsive barrier at larger separations. We studied the properties of this barrier, via measurements of the initial rate of large-particle aggregation. Real-time video microscopy, with spatial resolution at the level of single particles, allowed to determine the time evolutions for singlet, doublet and triplet number densities. By comparison to Smoluchowski theory, characteristic times were extracted and translated into stability ratios. A good correspondence with hard sphere behavior was found. 2) We also studied suspensions consisting of silica spheres, to which a non-adsorbing polymer was added to effect weak particle-aggregation. Using a solvent mixture, the refractive index of the particles could be closely matched, so as to allow microscopic observations deep into the suspension. Also the particle mass-density was matched, thus allowing long observation times without interference from sedimentation or creaming of particles (aggregates). Use of a confocal microscope allowed to characterize the aggregates via their contour-area distributions as observed in the focal plane. The aggregation process was followed from the initial state, until a steady state size distribution was reached. On varying polymer concentration and shear rate, it was observed that the steady-state aggregate size became larger with polymer concentration, and smaller with shear rate. This demonstrates that the size of the aggregates is governed by a subtle balance between cohesive forces caused by the polymer, and rupture forces associated with the flow.

Monday 4:00 Grand Station I SM11

Rheology and microstructure of sterically stabilized, acicular precipitated calcium carbonate dispersions and the shear thickening behavior

Ronald G. Egres and Norman J. Wagner
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There are numerous technological applications, such as in the coatings industries, for colloidal dispersions containing non-spherical particles such as clays and pigments. However, despite many literature reports of the rheology of such materials, to date there is no complete, quantitative elucidation of the influence of particle shape anisotropy on the rheological response of concentrated colloidal dispersions. Here we report a rheological and microstructural investigation of dispersions of sterically-stabilized, acicular precipitated calcium carbonate (PCC) particles having average aspect ratios of 2:1, 5:1 and 8:1. The effects of particle shape on the low shear viscosity, shear thinning behavior, and onset of shear thickening is explored by comparison to model, hard-sphere dispersions. It is demonstrated that particle alignment both at rest and under flow quantitatively and qualitatively alters the rheological response. The experimental results demonstrate that increasing particle aspect ratio leads to enhanced shear thickening at much lower particle concentrations than observed in comparable suspensions of spherical colloidal particles. Flow small angle neutron scattering (SANS) measurements of semi-dilute and concentrated anisotropic particle dispersions demonstrate that nematic-like long-axis orientation with flow direction is maintained throughout both the shear thinning and shear thickening regimes for dispersions exhibiting both continuous and discontinuous shear thickening. The onset if shear thickening is found to depend on a critical stress that is nearly independent of the particle volume fraction over the range investigated. These results are compared to recent micromechanical models to elucidate the mechanism of shear thickening in suspensions of anisotropic particles.

Monday 4:25 Grand Station I SM12

Rheological properties and flow-small angle neutron scattering of stable dispersions of nanoparticles at high shear rates

Young S. Lee and Norman J. Wagner
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It is well established that suspensions of particles from microns in size down to particles of the order of ~100nm have been observed to undergo a transition to a shear-thickened state at appropriately high shear stresses. However, the lower limit of particle size whereby reversible shear thickening can be observed has not been established. In this work a model dispersion of stable, silica nanoparticles (30nm, Clariant) in a viscous, Newtonian solvent (ethylene glycol) is explored using conventional rotational rheometry and a high shear rate cone. The shear rheology of charge-stabilized and polymer-stabilized colloidal suspensions is reported out as a function of the particle volume fraction. The results are compared to previous model system studies on colloidal dispersions and to micromechanical models that relate the physical parameters of the system, which are independently measured, to the rheological response. Reversible shear thickening is observed at very high shear rate after a strong shear thinning at the intermediate shear rate. The measured transition stresses for shear thickening compare well to theoretical predictions. Flow-small angle neutron scattering measurements both in the radial and tangential orientations show a pronounced shear-induced anisotropy near the shear thickening transition that is consistent with the hydrocluster mechanism of reversible shear thickening. The addition of adsorbing polymer (polyvinyl alcohol) is observed to systematically shift the low shear viscosity, the onset of shear thinning, and the transition to shear thickening in agreement with current modeling.

Monday 4:50 Grand Station I SM13

Kinematic shock waves in colloidal suspensions

Maria Kilfoil[1] and David Weitz[2]
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We observe what appear to be kinematic shock waves in a narrow window of gels of weakly attractive colloidal particles as the gels undergo a delayed collapse under gravity. These waves are easily visible by eye and appear as local high-density (or high contrast) packets moving upwards against gravity and against the flow due to the sedimenting particles. We observe this phenomenon in suspensions prepared with monodisperse colloidal silica particles with polymer present in the suspending fluid to induce an attraction between the particles. This behavior is seen only in some component mixtures; it is completely reproducible in these samples. Its origin may involve an interplay between the inter-particle interactions and the nature of the flow while the particles sediment.

Monday 5:15 Grand Station I SM14

Direct visualization of shear-induced colloidal crystallization by confocal laser scanning miscrscopy

Tesfu Solomon and Michael Solomon
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The crystallization of colloidal particles into structures with three-dimensional periodicity is the basis of one method to create materials with a photonic band gap. Yet, to apply colloidal self-assembly in this way, large single crystals with low defect density are required. Application of shear flow to an initially polycrystalline material can yield larger crystallites. The shear-induced ordering of nearly hard sphere colloids has been extensively studied by means of light scattering (Ackerson and Pusey, Phys. Rev. Lett., 61, 1033 (1988)); however, direct visualization by means of confocal laser scanning microscopy (CLSM) allows the new possibility of studying the evolution of grain boundaries and other defect structures that mediate shear-induced crystallization. We study these properties in concentrated suspensions of nearly monodisperse sterically stabilized silica colloids of diameter approximately 1 mm dispersed in a density and refractive index matched solvent mixture. By means of CLSM, we observe the three-dimensional structure of suspensions subjected to oscillatory shear flow of varying strain rate and amplitude. Qualitatively, we find that shear flow induces nucleation and growth of colloidal crystals in the initially amorphous suspensions. The pair correlation function and local bond orientational parameters are extracted from the CLSM image volumes by means of quantitative image processing. The strain rate and amplitude dependence of these measures of local ordering are quantified and discussed for volume fractions within the coexistence region.

Symposium VF
Viscoelastic Flows and Instabilities

Organizers: Jonathan Rothstein and Bamin Khomami

Monday 1:30 Grand Station III VF6

Dilute polymer flow incorporating slippage and polymer migration: Model formulation and predictions

L. Pamela Cook[1] and Lou Rossi[2]
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In this talk a model which includes both slippage effects and polymer migration effects will be presented. This model incorporates features of the higher order stress models (see Bhave, Armstrong, Brown: Beris and Mavrantzas) as well as features of the Johnson-Segalman model. The molecular model, a bead spring dumbbell model, will be presented showing clearly where new terms arise. The predictions of the model in shear flow will be presented. The ultimate goal is to predict shear banding in polymer flows and in addition the sudden apparent-viscosity drop and hysteresis under stress increments as observed in experiments. Stability characteristics of the solutions will be

presented. The inclusion of the higher order stress terms in the model, that is the coupling of the polymer stress equation with the number density equation, does in fact provide some selection mechanism for the nonuniqueness, under stress controlled experiments, as seen in the Johnson-Segalman mode

Monday 1:55 Grand Station III VF7

Flow stability of sparsely branched metallocene-catalyzed polyethylenes

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Chemical Engineering, Virginia Tech, Blacksburg, VA 24061

Metallocene catalyzed polyethylenes typically have narrow molecular weight distributions (MWD) which lead to a number of processing instabilities such as surface melt fracture at low shear rates, the onset of slip-stick melt fracture at low shear rates, and the onset of draw resonance at low draw ratios. Long chain branching (LCB) at levels less than one branch per chain is known to have a significant effect on the shear and extensional rheology of polyethylenes. We find that sparse LCB also has a significant effect on the extrusion and drawing stability of these polyethylenes, and it can be attributed to the effect that LCB has on the onset of shear-thinning and extensional strain hardening. The effects are noticeably different than those caused by broadening of the MWD. The results suggest that predicting stability behavior cannot just be approached from traditional linear or even non-linear stability analysis as relaxation times alone cannot account for the observed behavior. The extensional behavior plays a key role especially in situations where the flow is dominated by shear-free deformation.

Monday 2:20 Grand Station III VF8

The relationship of pressure sensitive adhesive rheology to high speed label converting processes

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Pressure sensitive adhesives (PSA's) are used in a variety of label products. Their performance depends on bulk adhesive properties as well as interfacial factors between the adhesive and adherend. PSA's are viscoelastic materials that are typically characterized by tack, peel and shear properties. Dynamic mechanical analysis can be applied to relate performance properties of PSA's to bulk adhesive properties. For example, a common criterion for maximum tack of PSA's at room temperature is that the T_g should be between –10 and +10°C and the storage modulus at ambient temperature should be between 5×10^4 and 2×10^5 Pa.

Several processes are important in the production of PSA labels including coating and drying of liquid adhesive on wide webs, slitting of rolls, stripping of release liners, guillotine cutting and die cutting. A major problem with slitting, guillotine cutting and die cutting is gumming of knives and dies with adhesive resulting in cuts that are not clean.

To identify the adhesive bulk properties that are important for improving these converting processes, dynamic and storage modulus values were determined for various adhesives using a Rheometrics RMS 800 Mechanical Spectrometer equipped with 25 mm parallel plate geometry. Measurements were carried out at ambient temperature over a frequency range of 0.1 to 100 radians/second. Trials at label converters demonstrated that adhesives having a G' greater than 1×10^6 Pa at 100 radians/second exhibit less gumming of knives and dies. This is consistent since die cutting and guillotine cutting are high frequency processes. It was also important to have G' less than 2×10^5 Pa at 0.1 radians/second in order to maintain adequate adhesive tack properties. Tack of a PSA depends on viscous flow of the adhesive when it comes in contact with a surface and this is believed to relate to the adhesive storage modulus at low frequency.

Monday 2:45 Grand Station III VF9

Persistence of straining and flow classification

Roney L. Thompson and Paulo R. Souza Mendes
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Astarita proposed in 1979 a local and objective criterion to classify flows. His criterion is not restricted to MWCSH, and is essentially an attempt to quantify the stress-relieving rotation experienced by the flowing material. Huilgol analyzed Astarita's work and in 1980 showed, through examples, some inconsistencies which rendered it useless as a general flow criterion. The present work revisits Huilgol's examples and discusses in detail the underlying physics that make Astarita's criterion to fail for certain flows. This analysis leads to a new criterion for flow classification involving the concept of persistence of straining. A key kinematic entity introduced in the proposed criterion is the pi-plane, a plane that is normal to the relative-rate-of-rotation vector. For a more comprehensive criterion, other parameters are needed in addition to a persistence-of-straining parameter. One of them is a measure of the deformation rate in the pi-plane. Although emphasis is given to isochoric motions, a compressibility parameter is also introduced to encompass non-isochoric flows. The proposed kinematic criterion is local, frame-indifferent and is not restricted to particular classes of flows. Its robustness is shown through detailed analyses of some representative flows.

Monday 3:35 Grand Station III VF10

Structure formation in drag reducing polymer solutions

Matthew Liberatore[1] and Anthony J. McHugh[2]
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Rheological and rheo-optical characterization of polymer solutions which exhibit drag reduction in turbulent flow, via injection or as a polymer "ocean", have been examined. Aqueous solutions of partially hydrolyzed polyacrylamide, polyacrylamide, and polyethylene oxide of two to five million molecular weight have been studied in the concentration range of 100 to 4000 ppm by weight. Experimental protocols included rheological and rheo-optical characterization under simple shear flow, and molecular weight analysis by chromatography. A Couette device capable of shear rates up to 8000 s^{-1} was used to provide dynamic and steady state viscosity, transmittance, birefringence, dichroism and small-angle light scattering patterns. Comparisons of Mie Theory with measured turbidity suggest the size of flow-induced structures ranging from clusters of entangled chains to almost completely phase-separated droplets. Time-dependent concentration fluctuations observed in the flow-shear plane are compared with theoretical predictions from the Helfand-Fredrickson model and others. Molecular weight degradation has also been monitored for a variety of shear and turbulent flow histories. These results are compared against turbulence measurements that relate drag reduction directly to structure formation. Current work will also be correlated with earlier results from our laboratory showing that, depending on concentration, solution ionic strength, and shear rate, either pseudo-reversible, or irreversible aggregate formation and precipitation occur above a critical shear rate.

Monday 4:00 Grand Station III VF11

The effect of rheological properties in viscoelastic turbulent channel flow

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We investigate the moderate to high drag reduction region in viscoelastic turbulent channel flows through Direct Numerical Simulations (DNS). By using high accuracy, spectral methods based, numerical simulations our goal is to elucidate the drag reduction mechanisms. In particular, in this work, we seek to find under which conditions high drag reduction values can be accomplished as well as to study the effect of the variations of the various rheological parameters of the problem.

Our previous simulations have shown that the polymer induced drag reduction is insensitive to the friction Reynolds number keeping all the other rheological parameters the same. However, the structure of the flow in the boundary layer converges into an asymptote only for values of the friction Reynolds number higher than 395. Also, we have found that most of the changes due to the viscoelasticity (Weissenberg number) are taking place primarily in the boundary layer, and are reaching an asymptote when the friction Weissenberg number approaches a value around

50-60 (for the FENE-P constitutive model). Thus, in the present work, we focus our analysis at these Reynolds and Weissenberg number values.

The polymer stress is modeled by using three different constitutive equations: (a) the FENE-P model with maximum extensibility parameter up to 95 (b) the OLDROYD-B model and (c) the GIESEKUS model with a mobility parameter so that to match the maximum extensional viscosity of the FENE-P model.

The effect of varying rheological parameters for the above used constitutive models, (maximum extensibility parameter, mobility parameter, maximum extensional viscosity), as well as the solvent viscosity ratio, will be presented in the drag reduction and the turbulent statistics. Results on higher order statistics quantities the Reynolds stresses and the energy spectra will also going to be shown.

Monday 4:25 Grand Station III VF12

Interpretation of Virk phenomenology for polymer turbulent drag reduction

Ronald G. Larson and Anshuman Roy
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The Virk phenomenology for polymer turbulent drag reduction, which predicts an upward parallel shift *S+* in the mean velocity profile due to added polymer is herein explained using scaling arguments for maximum eddy length and time scale above which the polymer can no longer affect turbulent structure. We propose that if the polymer is to affect the dynamics of the flow, its effect must be felt by the largest eddies that exist at a given distance *y+* from the wall, measured in turbulence units. Since with increased distance from the wall these largest eddies both grow in size and become more sluggish, they eventually either become too big or too slow for polymer to influence them. The distance from the wall at which this occurs depends on polymer molecular weight and concentration. Using an ad hoc expression for the von Karman constant *k* in the formula for the mean streamwise velocity gradient that deviates from its Newtonian value only when the length and time scale conditions are both satisfied, we develop a formulation that captures the observed increase in slope of the mean velocity profile that is confined to the polymer buffer layer, and reproduces the upward parallel shift *S+* in the limiting case of $Tr >> 1$ and $Wi/Wi^* >> 1$.

Monday 4:50 Grand Station III VF13

Polymer chain dynamics and turbulent bursts: A mechanism of drag reduction

Vijay Gupta, Changfeng Li, Radhakrishna Sureshkumar, and Bamin Khomami
Washington University, Saint Louis, MO

Polymer chain dynamics in turbulent channel flows are examined by Brownian Dynamics simulations utilizing FENE and FENE-P dumbbell models. The influence of maximum extensibility and relaxation time on the chain dynamics in the viscous sublayer, buffer layer and the turbulent core is examined. It is shown that the quantitative differences between the predictions of the (continuum-level) FENE-P and (stochastic) FENE models for the average chain extension in the viscous sublayer and the buffer layer can be practically eliminated by renormalization of the maximum extensibility parameter. Recently, direct numerical simulations (DNS) of turbulent channel flow of viscoelastic polymer solutions have revealed that drag reduction (DR) is closely related to the interaction between the quasi-periodic streamwise vortices present in the turbulent flow and polymer chains. We will show that for values of DR up to 40%, the probability distribution function (PDF) for the chain extension shifts progressively towards larger values of extension with increasing DR. However, even for DR of approximately 40%, the PDF exhibits a long tail indicating that a significant fraction of polymer chains are relatively unstretched. Flow visualization studies based on DNS indicate that this can be explained by the fact that chains on the surface of the quasi-streamwise vortices undergo larger extension compared to those farther from it. The enhanced extension increases the extensional viscosity of the solution and stabilizes the streamwise vortices. Consequently, the frequency of turbulent bursts (associated with the lift up of streamwise vortices) and ejections (that result in the mixing of near wall fluid with fluid near the center of the channel) is significantly reduced. This causes a reduction in the overall turbulence production. A mechanism of turbulent drag reduction inspired by the above findings will be presented.

Monday 5:15 Grand Station III VF14

Interactions between polymer rheology and turbulent coherent structures in drag-reducing fluids

Philip A. Stone and Michael D. Graham
University of Wisconsin-Madison, Madison, WI

A key structural observation of drag-reducing polymer solutions is that the structures of the buffer region are modified. To better understand how polymer additives affect these structures, we make use of the "exact coherent states" (ECS) recently discovered in plane Couette and Poiseuille flows. The ECS are traveling wave solutions to the Navier-Stokes equations that capture the kinematics of the buffer region and underlie the dynamics of the turbulent coherent structures. The optimal size for the ECS also closely matches the streak spacing in the buffer region. Starting with the Newtonian ECS, we find similar, viscoelastic, nonlinear states using the FENE-P dumbbell model to calculate the polymer stress. The modification of the ECS by the polymer closely mirrors observations from experiments: Reynolds shear stress decreases, wall-normal fluctuations are suppressed while streamwise fluctuations are enhanced, and drag is reduced. The structural mechanism underlying these changes is presented. We also assess the use of the FENE-P dumbbell in this study by comparing it to Brownian dynamics simulations of more realistic bead-spring-chain models in the ECS flow field. Although the FENE-P model does not capture the hysteresis in stress seen in the bead-spring-chain models, it does qualitatively capture the spatial variations in the polymer stress.

Symposium RS
Rheology of Solids and Near-Solids

Organizers: Greg McKenna and Tony McHugh

Monday 1:30 Grand Station IV RS6

Physical aging of an epoxy glass-former after one- and two-step relative humidity and temperature jumps

Yong Zheng, Rodney D. Priestley, and Gregory B. McKenna
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One cause of the long-term dimensional changes in glassy polymers is the gradual evolution of the viscoelastic behavior through aging processes in the glassy state. Many applications involve changes in relative humidity (RH), under which the materials exhibit aging processes that may differ from those in constant (RH) conditions. Work done by Zheng and McKenna has shown that the dilatation response after relative humidity jumps has a similar phenomenology to, but different kinetics from that obtained from temperature jumps. In the present work mechanical creep tests are performed during structural recovery of the sample after relative humidity and temperature jumps using Struik's sequential loading protocol. The tests include intrinsic isopiestics, memory effect, and asymmetry of approach, which are indirectly represented by the shift factors of the retardation times. The creep compliances as a function of time are also analyzed by the KWW stretched exponential function to estimate the retardation time. In addition, a comparison will be made describing the similarities and differences of creep responses between relative humidity and temperature jump experiments. These results are compared with results from earlier volume measurements and tentatively explained within the energy landscape paradigm.

Monday 1:55 Grand Station IV RS7

Structural recovery response of an epoxy resin after carbon dioxide pressure-jumps: Intrinsic isopiestics, asymmetry of approach and memory effects

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The normal approach to physical aging or structural recovery experiments is to perform temperature jump experiments in which one removes the sample from an equilibrium condition (normally above the glass temperature) to a non-equilibrium condition and follows the return of the sample towards equilibrium. Here we examine the results of performing similar experiments, but now by changing the "chemical activity" of the surrounding

environment through changes in carbon dioxide pressure (P_{CO2}). Because polymers can be plasticized by CO_2, it was anticipated that the results of the experiments would be similar to the results from temperature jump-experiments. We have developed experimental techniques that permit the measurement of the changing volume after such jumps and will present results of the structural recovery for thin films (40 ~ 60 micron) of an epoxy after P_{CO2}-jump experiments under thermal conditions from above the "glass" P_{CO2} to below it. These experiments are classed as intrinsic isopiestics, similar to the Kovacs classification of intrinsic isotherms. Similarly, two-step experiments show the memory effect and comparisons of up-jump and down-jump tests show a strong asymmetry of approach behavior. Finally, because the volume changes associated with changes in plasticizer content of the polymer can be significantly larger than those associated with changes in temperature, it is important to establish the limits of applicability of current models, such as the TNM or KAHR models to the description of these experiments. This will also be discussed.

Monday 2:20 Grand Station IV RS8

Rheology of cohesive granular materials: Flow down an incline

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The study of cohesive granular media is fundamental to the exploration of sand in a geophysical context where small quantities of a wetting fluid generate cohesive stresses within the granular aggregate. We have performed large-scale particle simulations of cohesive and non-cohesive granular media in three dimensions to study the dependence of the rheology of the granular material on the inter-grain cohesion. Here we report on the steady-state flow of the granular material down an incline and examine the depth dependence of the particle packing fraction, and velocity profile in the direction of flow. We compare our numerical results to simple scaling theories of granular flow.

Monday 2:45 Grand Station IV RS9

Forces in granular hopper flow

James W. Landry and Gary Grest

Sandia National Labs, Albuquerque, NM 87108-1415

Inter-particle and particle-wall forces in granular flow out of a hopper are explored using large-scale 3D molecular dynamics simulations. The simulations begin by pouring particles into a cylindrical container or silo. The vertical stresses become depth-independent for deep piles and we compare these stress depth-profiles to the classical theory of Janssen. The majority of the tangential forces for particle-wall contacts are found to be close to the Coulomb failure criterion, in agreement with the theory of Janssen, while particle-particle contacts in the bulk are far from the Coulomb criterion. Flow is initiated by opening the bottom of the silo. We examine the transition from a frictional regime at the onset of flow to a steady-state collisional flow regime at the mouth of the hopper. The existence and prevalence of force chains are examined for a range of flow rates and geometries. The onset of jamming is investigated in depth.

Monday 3:35 Grand Station IV RS10

Characterization of cured and uncured highly filled polymers using the new SER extensional rheometer fixture

Martin Sentmanat

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The cured and uncured extensional deformation behavior of a series of polymers of varying macrostructure, filler loading and content was characterized with the use of the new commercially available SER extensional rheometer fixture. The miniature SER unit has been specifically designed for use as a fixture on a variety of commercially available rotational rheometers and can be accommodated within the smallest of environmental chambers. The uniaxial extension data indicate that even subtle differences in polymer macrostructure, filler content and dispersion are easily distinguishable with this robust instrument.

Monday 4:00 Grand Station IV RS11

On the implementation of time-temperature superposition

Shyni Varghese and Davide A. Hill
Dept. of Chemical and Biomolecular engineering, University of Notre Dame, Notre Dame, IN 46556

We discuss a mathematical method that can aid one in constructing master-curves for dynamic (oscillatory) moduli through time-temperature superposition. The technique takes advantage of both the value of the loss tangent and its slope against frequency. In cases where the loss tangent is monotonic with frequency, the master-curve can be produced automatically with no input from the operator. For systems that exhibit loss tangent peaks (e.g., due to a rubbery-to-glass transition) the method provides guidelines on how to properly shift the data. Examples will be discussed involving artificially-generated as well as experimental data for polymer melts and thermoset resins, the latter both above and below the glass transition temperature.

Monday 4:25 Grand Station IV RS12

A rheological investigation of the phase transition behaviour of thermoplastic polyurethanes

Dario Nichetti[1] and Nino Grizzuti[2]
[1]Chiorino SpA, Biella 13900, Italy; [2]Department of Chemical Engineering, University of Naples, Napoli 80125, Italy

The phase transition behaviour of thermoplastic polyurethane block copolymers has been investigated by coupled rheological/DSC techniques. Polymers are obtained by polymerization of 4,4'-diphenylmethane diisocyanate (MDI) with polybutylene adipate (PBA) ester with 1,4-butandiol (BDO) as the chain extender. Oscillatory flow and step strain tests have been performed by means of a controlled strain rotational rheometer with parallel plate geometry. The kinetics of micro-phase transition have been followed under both isothermal conditions (crystallization from the melt), and constant temperature rate heating ramps (melting). The rheological results have been compared with those obtained by more traditional calorimetric techniques (DSC) under the same thermal histories. It is shown that rheological measurements can give additional (and, in some cases, more accurate) information with respect to that obtained from the more classical thermal analysis. In particular, the time evolution of the viscoelastic moduli indicates that phase transition takes place through three different stages: induction, crystallization/phase separation and structural reorganization of hard domains. Repeated step strain tests during the phase separation process have also allowed to determine a critical gel point behaviour during both isothermal crystallization from the melt and non isothermal melting. Rheological results, however, show that the characteristics of the critical gel strongly depend upon the applied thermal history.

Monday 4:50 Grand Station IV RS13

Cooperative dynamics in glass-forming liquids

Brian M. Erwin, Ralph H. Colby, and Sanat K. Kumar
Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802

Computer simulations show a length scale for cooperative motion in glass-forming liquids that grows rapidly as temperature is lowered below a caging onset. We present evidence for this caging onset from rheology and dielectric spectroscopy literature data. We also demonstrate how viscosity, dielectric relaxation time, and molecular probe data below the caging temperature can be interpreted using the length scale for cooperative motion, which appears to diverge at a temperature below the glass transition temperature.

Monday 5:15 Grand Station IV RS14

Role of molecular tacticity on the crystal structure and plastic deformation behavior of semi-syndiotactic polypropylenes

Michael Sevegney[1], Gautam Parthasarthy[1], Rangaramanujam M. Kannan[1], and Allen Siedle[2]
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Novel synthesis methods have made it possible to make polymers with well-defined composition, tacticity, architecture and molecular weight. This provides a tremendous flexibility to engineer products that have tailored properties at the molecular and nanostructural levels. However, quantifying and relating responses at these length

scales to macroscopic properties is still a challenging task. Metallocene catalysis enables synthesis of polymers with well-defined tacticity, thereby providing materials with a wide range of properties, all from same monomer. However, understanding the role of tacticity at the molecular level, on the crystallization, mechanical, and flow behavior has been a challenge.

We are studying custom synthesized semi-syndiotactic polypropylenes (ss-PP) with varying degrees of 'syndiotacticity', ranging from nearly atactic to nearly syndiotactic. . These materials have been custom-synthesized using asymmetric, bridged cyclopentafluorenyl catalysts, and characterized using NMR, modulated DSC, mechanical testing, AFM, rheology, and rheo-optical FTIR spectroscopy, WAXD and Raman spectroscopy. In the semi-syndiotactic PPs, the rate of crystallization is significantly slower that s-PP, and the crystal structure is very different. These materials appear to form a meso-phase consisting of trans-planar and/or helical chains, depending on regularity and annealing conditions. In the highly polymorphic, highly syndiotactic s-PPs, in the plastic deformation region, there appears to be a gradual transition in macromolecular conformation from helical to trans-planar. The trans-planar chains appear to form a meso-phase, before forming a well-defined crystalline phase at even higher strains. The nature of the conformation transition and the 'elastic' behavior (in the plastic region) appears to be strongly dependent on tacticity, temperature, and the orientation in the amorphous, meso-phase and the crystalline region, and are explored using rheo-FTIR and Raman spectroscopy.

Symposium MM
Microrheology, Microfluids and MEMS

Organizers: Gerry Fuller and Kalman Migler

Monday 1:30 Grand Station V MM6

Flow control in microenvironments based on micellization in triblock copolymer solutions

Boris Stoeber[1], Dorian Liepmann[2], and Susan J. Muller[3]

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Thermally responsive fluids are very useful materials for flow control in microenvironments due to the small timescale of heat propagation compared to the timescale for convective transport phenomena at this small scale. Here, we consider dilute aqueous solutions of certain (Polyethylene oxide)$_x$-(Polypropylene oxide)$_y$-(Polyethylene oxide)$_x$ triblock copolymers which undergo a reversible phase change at elevated temperatures from an isotropic micelle structure to a cubic soft crystal matrix. The rapid, reversible gelation of these materials upon heating results in an increase of their effective viscosity. This transition, which depends upon the molecular weight of the polymers as well as their concentration, is examined as a means of flow control in microfluidic devices. Microchannels with integrated electric heaters were fabricated and valving is demonstrated using a dilute aqueous solution of the triblock copolymer as the working fluid. Flow visualization and digital particle image velocimetry confirms that heating of the solution results in gel formation in the vicinity of the heater and blocks the channel. Gel formation results in flow cessation within 67 ms. Under certain conditions gel formation of triblock copolymers in microchannels has been observed due to viscous heating in the regions of high shear close to the channel walls. This can lead to a complete blockage of the flow channel, or it can result in temporal instabilities as shown through video imaging.

Monday 1:55 Grand Station V MM7

Strategies for passive fluid mixing in microchannels

Jai A. Pathak[1], David Ross[2], and Kalman B. Migler[1]

[1]Polymers Division, NIST, Gaithersburg, MD 20899-8544; [2]Process Measurements Division, NIST, Gaithersburg, MD 20899-8362

Mixing in micro-channels is a challenge as flows in these systems are low Reynolds number flows, and diffusion requires long channel lengths to bring about mixing. Inspired by the recent reports of elastic turbulence in flows of high polymer solutions, we exploit elasticity driven turbulence to mixing in microchannels. We quantify the effects of elastic turbulence on mixing efficiency, and extend our work to studying the effects of improved mixing on a model chemical reaction. In addition, we investigate the effects of channel geometry on the mixing of fluids in our microchannels, which are fabricated by laser ablation of polymeric substrates, and subsequent sealing by a lid made of another polymeric material.

Monday 2:20 Grand Station V MM8

Migration of a complex structured particle in Newtonian fluid

Masato Makino and Masao Doi
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We provide a theory and simulation for a complex structured rigid particle in Newtonian fluid. The velocity V and the angular velocity Ω of a rigid particle subjected to force F and torque T in a velocity field $V = V_0 + \Omega_0 \times r + E r$ is written as $V - V_0 = aF + bT - g{:}E$ and $\Omega - \Omega_0 = bF + cT - h{:}E$. where a, b, c, g, h are the tensors determined by the shape of particle. In this study, we examine the effect of skew on the translational motion of particles.

(1) Sedimentation of propeller particle. When an elliptic particle settles down along the z direction, it moves with constant velocity in the x-y plane. For a propeller-like particle, we found that its motion in the x-y plane remains in the finite region. There is no propeller-like particle migration in the x-y plane.

(2) Separation of the chiral particle under the simple shear flow. We found that we can separate the chiral particles using the simple shear flow. The efficient of the separation depends on the shape of the particle.

Monday 2:45 Grand Station V MM9

From two-point microrheology to cell mechanics

John C. Crocker, Brenton D. Hoffman, and Gladys Massiera
Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA

In recent decades, cell biophysicists have developed several different methods for probing the rheology of the cytoskeleton in living cells. A major goal of the field is to develop a more physical "cell mechanics" model relating cellular rheology and function to the cytoskeleton's molecular constituents, described by biochemists and single-molecule biophysicists in ever increasing detail. The physical models proposed to date—the sol-gel, tensegrity and soft glassy rheology models—all have both merits and inadequacies. Recently, two-point microrheology has yielded a wealth of new information regarding the spatial, temporal and statistical distribution of endogenous strain fluctuations in the living cytoskeleton. Such data provides an increasingly clear picture of microscopic stress, rearrangement and rupture events and how these relate to cell rheology and motility. By combining aspects of different cell mechanics models, an intuitive explanation of our data emerges, which we shall discuss.

Monday 3:35 Grand Station V MM10

A microbubble method to measure biaxial creep of nanometer thickness films

Paul A. O'Connell and Gregory B. McKenna
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Performance of materials at the nanometer size scale has become a subject of considerable interest in recent years. Yet, methods of making measurements of the viscoelastic response of materials with nanometer size dimensions have not been well developed or are plagued by issues surrounding contact mechanics. Here we describe a novel approach in which a spin cast polymer film can be deposited over a porous template. Because the pores are through channels, the film forms a thin membrane over the channel. We built a fixture to apply a pressure across the template, hence inflating the membranes that cover the channels. Placement of the template into the atomic force microscope permits the imaging of the inflated membranes as a function of time after the application of the known pressure. By measuring the shape of the inflated bubble, we can determine the strain and the curvature of the membrane. Combined with the knowledge of the pressure, we can calculate the stress at the pole of the membrane and, therefore, the biaxial compliance. By monitoring the bubble shape as a function of time, we determine the biaxial creep compliance, which is six times the shear creep compliance for an incompressible material. Here we describe measurements using the “nanobubble inflation” device in which we determined the creep compliance of films of poly(vinyl acetate) at temperatures between ambient and 60°C. The film thicknesses vary from approximately 50 to 300 nm. We discuss the applicability of time-temperature superposition to these films and examine the possibility of using time-film thickness superposition as well. The latter principle should apply if the glass transition of the film decreases with decreasing film thickness (as has been claimed by some researchers) and if the shape of the creep compliance curve is unaltered by the nanometer size scale being investigated.

Monday 4:00 Grand Station V MM11

Surface dynamics in semi-crystalline polymer films

Keiji Tanaka[1], Atsushi Sakai[1], Atsushi Takahara[2], and Tisato Kajiyama[3]
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Polymer surface plays an important role in many technological applications. To design highly functionalized polymers, the systematical understanding of surface structure and physical properties is important. So far, we have studied on amorphous surface, and learned that the surface was different from the corresponding bulk, structurally and dynamically. Of such, it is interesting that chain mobility at the surface is much enhanced in comparison with the bulk. However, little information has been known on the surface in semi-crystalline polymers. In this study, we discuss about surface aggregation states and dynamics in semi-crystalline isotactic polypropylene (iPP) film. The iPP was melted on a Si wafer and then immediately quenched to 273 K. The film thickness was set to be about 1 mm. Surface dynamics was examined by lateral force microscopy (LFM). Since the origin of lateral force is closely related to dynamic loss modulus, E'', temperature-lateral force curve corresponds well to temperature-E'' relation at the surface. For the bulk iPP specimen, the a-absorption peak corresponding to the segmental motion was discerned at 285 K. At the surface of the intact iPP film, a similar peak was also observed at around 250 K. However, the peak was disappeared after the surface treatment with $KMnO_4$ etchant so that the amorphous region on the surface would be stripped off. This means that the peak comes up with a relaxation process in the surface amorphous region. Then, we examined the activation energy of the surface relaxation process. The obtained value was 230 kJ/mol, being equivalent to the reported value for the a-relaxation process at a typical amorphous surface. The surface a-relaxation process was observed at a temperature remarkably lower than the corresponding bulk one. In addition, the activation energy for the surface a-relaxation was lower than the bulk value. Hence, it seems reasonable to conclude that surface molecular motion is more vigorous than bulk one even for the semi-crystalline iPP film.

Monday 4:25 Grand Station V MM12

Nanorheology using the atomic force microscope

Patricia M. McGuiggan[1] and David J. Yarusso[2]
[1]Polymers Division, NIST, Gaithersburg, MD 20899; [2]Commercial Graphics Division, 3M, St Paul, MN

An atomic force microscope (AFM) is used to measure the loss tangent, tan d, of polymeric films of varying stiffnesses. For the measurement, the sample is oscillated normal to the surface and the response of the cantilever resting on the polymer (as measured via the photodiode) is monitored. Tan d will be measured as a function of frequency as well as amplitude. The results will be compared to bulk measurements using a dynamic shear rheometer.

Monday 4:50 Grand Station V MM13

Rheology and birefringence at high shear rates

Khaled S. Mriziq[1], Mark D. Dadmun[2], and Hank D. Cochran[3]
[1]Physics, University of Tennessee, Knoxville, TN 37996; [2]Chemistry, Uinversity of Tennessee, Knoxville, TN 37996; [3]Chemical Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6181

We demonstrate a novel apparatus to investigate rheological and structural properties of polymer melts and solutions at high shear rates. Most common, experimental techniques available for studying the rheological and structural properties are cone-plate and Couette geometries. However, these techniques are limited to moderate shear rate because of the difficulty in removing the viscous heat. The present apparatus utilizes the geometry of magnetic disk-drive system in which a thin film is sheared between optically transparent disk and slider interfaces at relatively low sliding speed. The rheological properties of the polymer film can be obtained by measuring the stresses on the slider, and the sample's birefringence and extinction angle (and other optical measurements) can be obtained from light intensity to study the structure. Capabilities of the instrument are demonstrated through rheological and optical measurements on perfluoropolyether lubricant films in shear rates of range of 10 s^{-1} and 10^6 s^{-1}. The potential exists to extend the operating range to even higher shear rates using thinner films and higher sliding speeds. This, as well as study of narrow molecular weight cuts of perfluoropolyether lubricants, is the focus of continuing studies.

Monday 5:15 Grand Station V MM14

A novel rheometer plate fabricated using MEMS processes for accurate measurements of N_1 and N_2

Seong-gi Baek[1] and Jules J. Magda[2]
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A novel sensor plate was fabricated using microfabrication processes of Micro-Electro-Mechanical Systems (MEMS) to measure the first (N_1) and the second (N_2) normal stress differences at the same time. The sensor plate measures local pressures of a sample during shearing as a function of radial position, a pressure profile, with monolithically integrated miniature silicon pressure sensors at various radial positions. From the measured pressure profile, values of N_1 and N_2 are calculated directly using the well known equation. The local pressures were measured by a deflection of the silicon membrane in a sub micron range and thus no hole pressure error is involved. Current rheometers measure only N_1 from the vertical movement of a rheometer plate and there is a "compliance error" due to the vertical movement. A sophisticated and expensive transducer, the Force Rebalance Transducer, has been developed to counter balance or correct the compliance error. The sensor plate does not move vertically during measurement and therefore no compensation for the compliance error is needed. This sensor plate, which RheoSense, Inc. commercializes, can be used for various polymers from solutions to melts and is designed with flexibility so it is adaptable to various rheometers. The employed pressure profile measurement of the MEMS sensor plate offers advantages over conventional systems. These advantages are no gap change, a faster response time, and a higher accessible shear rate to name a few. Test results with a standard NIST solution (SRM-1490) showed that the MEMS sensor plate measures accurate pressure profiles, N_1, and N_2 inferred from the agreement between the N_1 values measured with the sensor plate and the certified values. The significance of this sensor plate, its advantages, fabrications, and the test results with polymers will be presented.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Grand Station I/II PL2

The nonlinear response of entangled polymers. Does theory explain all the facts?

Giuseppe Marrucci and G. Ianniruberto
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The linear behavior of entangled linear polymers appears to be described satisfactorily, at least in the monodisperse case, by the well known reptation theory, suitably refined with the contributions of chain-end fluctuations and constraint release. The latter mechanisms also explain the linear response of more complex molecular architectures, as generated by long branching. The situation changes considerably when theories are tested against the nonlinear behavior. First of all, new ingredients need to be introduced, notably chain stretching and, as recognized only recently, convective constraint release (CCR). More or less detailed models must then be (and have in fact been) developed that contain all these (linear and nonlinear) mechanisms. In all models, CCR solves the problem of the excessive shear thinning predicted by the basic tube theory at the onset of nonlinearity, while chain stretching is invoked to explain the response observed in faster flows. Here we summarize these recent developments, and critically discuss whether or not the mechanisms so far recognized are in fact sufficient to explain all, or most, of the available evidence in the nonlinear range.

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Tuesday 9:45 Grand Station I SM15

Stability of cocontinuous polymer blends

Jeffrey A. Galloway and Christopher W. Macosko
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55414

Cocontinuous polymer blends allow for unique combinations of properties, making them ideal for a numerous applications. One of the important challenges of producing immiscible blends with cocontinuous morphologies is stabilizing the non-equilibrium morphology to prevent coarsening and breakup of the domains. In these experiments, block copolymers were added to binary polymer blends and their effect on the blend formation and morphological stability during annealing was determined. The blends were characterized using rheological measurements and analysis of scanning electron microscopy images. Preliminary experiments have shown that block copolymers of intermediate molecular weight provided the greatest reduction in phase size during blending and the best stabilization during annealing.

Tuesday 10:10 Grand Station I SM16

Thermodynamic modeling of polymer blends with matrix phase viscoelasticity

Brian J. Edwards[1] and Marco Dressler[2]

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A Hamiltonian framework of non-equilibrium Thermodynamics is adopted to account for the effect of matrix phase viscoelasticity on the rheology of polymer blends with a droplet morphology. The system to be described in the talk can be envisioned as a viscoelastic matrix fluid with elastic modulus, G, which interacts with microscopically small droplets being dispersed throughout the matrix with a concentration, ϕ. The elastic modulus due to the presence of the interface, Γ, is related to the interfacial tension between the blend components. The blend is described in terms of the translational momentum density of the fluid and two contra-variant internal variables to account for the conformation of the polymer molecules in the matrix and the constant volume ellipsoidal droplets. A set of thermodynamically consistent time evolution equations for the system variables is derived which accounts for the influence of matrix viscoelasticity on droplet viscoelasticity and vice versa. This is achieved by introducing a phenomenological dissipative parameter, θ, which allows for a non-linear coupling of the internal variable describing the polymers in the matrix and the droplet shape tensor. The set of time evolution equations is solved for start-up and cessation of steady shearing flow, microstructure/rheology relationships are discussed, and a comparison with other constant volume models is made.

Tuesday 10:35 Grand Station I SM17

Shear behavior of attractive and repulsive emulsions: Relationship of attractive forces, negative normal stresses, and vorticity alignment

Alberto Montesi, Alejandro Peña, and Matteo Pasquali

Chemical Engineering, Rice University, Houston, TX 77005

This work compares the rheological behavior of attractive emulsions (in which drops flocculate or gel) and repulsive emulsions (in which drops remain separated) at different volume fractions of disperse phase. The physico-chemical properties (viscosity ratio, interfacial tension) of the two systems are matched, except for the droplet-droplet interaction energy. When the volume fraction of the disperse phase ϕ is below the hard sphere glass transition ($\phi_g < 0.58$) the attractive and the repulsive systems show very different shear thinning curves: while the viscosity is the same at high shear rate, the attractive emulsions show much higher low shear viscosity, clearly due to the presence of flocs. For this same reason, G' is much higher in attractive emulsions, that show measurable elasticity even when $\phi = 0.1$. At $\phi > 0.58$, the droplets in the emulsion become compressed and the interaction forces cease to influence the rheological properties. More interestingly, attractive emulsions show a peculiar behavior near the hard sphere glass transition, when droplets are caged indefinitely by their neighbors. The apparent viscosity decays with growing shear rate, then remains relatively constant in a range of shear rates, and then continues to decay. Moreover, the first normal stress difference N_1 transitions sharply from nearly zero to negative at the onset of the region of constant shear viscosity. In contrast, caged repulsive emulsions exhibit a monotonic viscosity decay; their N_1 is nearly zero until high shear rates, where it becomes positive. Microscopic observations of emulsions sheared between parallel plates reveal that the effects observed for the attractive emulsions are related to the formation of cylindrical flocs that align in the direction of the vorticity and undergo a movement that resembles that of rolling logs. Such microstructural development is absent in the repulsive emulsions, which do not show a viscosity plateau nor a negative N_1.

Tuesday 11:00 Grand Station I SM18

Extension of the Maffettone and Minale model to predict effects of high order in capillary number

Mario Minale

Dept. of Aerospace and Mechanical Engineering, Seconda Università di Napoli, Aversa, CE 81031, Italy

The Maffettone and Minale model (1998) for the deformation of a single Newtonian drop immersed in a Newtonian matrix has been extended to predict high order effect in capillary number (Ca). It is assumed that the drop shape is ellipsoidal both at steady state and during transients. The drop shape is, then, described by a second rank symmetric positive definite tensor denoted $\mathbf{S}$; it is deformed due to the competing actions of the viscous drag of the flow and

the restoring force exerted by the interfacial tension. The flow is completely described by the deformation velocity tensor **D** and the vorticity tensor **W**. In the original paper the vorticity tensor appears in the Jaumann derivative of **S** so to have a frame indifferent time derivative. The same formulation is kept in the model extension here presented. The extended model must account for high order capillary effects and it must properly recover the limits of small Ca numbers as Maffettone and Minale model does. We then propose to add to the evolutive equation for **S** terms obtained by combining the tensor **S** and the tensor **D**. To avoid to alter the small Ca limits the lowest order of the new terms must be Ca^2. Therefore in the first terms that can be added the tensor **D** must appear twice and the tensor **S** once. We have then considered the most general formulation where terms made by **S D D** are added and we imposed to preserve the determinant **S**, i.e., the drop volume. The predictions of the model well compare with experimental data and are able to catch phenomena that are missing in the original model as the drop widening during transients.

Reference: Maffettone PL and M Minale, *J. Non-Newt. Fluid Mech.*, **78**, 227-241 (1998).

Tuesday 11:25 Grand Station I SM19

Drop dynamics with non-Newtonian liquids under shear flow: Phenomenological model and experimental results

Pier Luca Maffettone[1], Francesco Greco[2], Stefano Guido[3], and Marino Simeone[3]
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Drop shape dynamics has been extensively studied for Newtonian liquid components. There are comparatively few studies on the non-Newtonian case. Here, we consider, both theoretically and experimentally, the situation where one of the two phases is a non-Newtonian liquid. The simple phenomenological theory is developed by assuming that the drop is always ellipsoidal, and by using simple invariance arguments to write down the dynamical equation for the drop shape. The model parameters are obtained in the limit of slow flows, where the non-Newtonian fluids become second order fluids, and the drop deformation is small. Predictions for large drop deformations and fast flows are then obtained without any additional parameter. Shear experiments are carried out with Boger fluids in a parallel plate apparatus equipped with an optical microscope. Drop shape is observed either along the vorticity axis or along the gradient direction. Stationary and transient flows are investigated for various rheological properties (viscosity ratio, elasticity) of the components. We found a good agreement between theory and experiments in all the cases considered.

Symposium VF
Viscoelastic Flows and Instabilities

Organizers: Jonathan Rothstein and Bamin Khomami

Tuesday 9:45 Grand Station III VF15

Modeling 3-D viscoelastic flows with free surfaces and interfaces

Xueying Xie, Kyriacos Zygourakis, and Matteo Pasquali
Chemical Engineering Department, Rice University, Houston, TX 77005

Free surface flows are present in a variety of processes such as coating, polymer processing, deformation of blood cells, etc. In a flow with free surfaces or interfaces, the flow domain is unknown a priori; thus, a mesh generation equation must be added to the problem equations to map the unknown domain onto a reference computational domain. Several mesh generation methods have been developed, chiefly elliptic mesh generation and domain deformation method. These methods have been applied successfully to 2-D free surface flows both with Newtonian (Christodolou and Scriven 1992, Sackinger et al, 1996) and non-Newtonian fluids (Pasquali and Scriven, 2002, Lee et al, 2003). 3-D free surface computations are still in their infancy because of the complexity of the free surface manipulation and the large-scale computations (e.g., Cairncross et al., 2000).

Here the domain deformation method is applied to model 3-D free surface flows; the viscoelastic response of the liquid is described by a general conformation tensor model. The DEVSS-G/SUPG Finite Element method is employed to discretize the problem equations into large set of non-linear algebraic equations, which are solved by the fully coupled Newton's method with analytical Jacobian. At each Newton step, the large-scale linear algebraic equations are solved by parallelized restarted GMRES method preconditioned by incomplete LU. Preliminary results are presented on the flow in a 3-D channel with a collapsible section and on the shear-induced deformation of a white blood cell traversing a narrow capillary.

Tuesday 10:10 Grand Station III VF16

A numerical study of viscoelastic free surface flows using the finite element method – Hele Shaw cell flows

Gandharv Bhatara[1], Eric Shaqfeh[1], and Bamin Khomami[2]
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A pseudo-solid domain mapping technique, based on a finite strain model, coupled with a DEVSS finite element formulation is applied to study the effects of viscoelasticity on free surface flows. The flow type analyzed is the displacement of a polymeric fluid in a Hele Shaw cell. The FENE-CR constitutive equation is used to model the flow. A Galerkin formulation is used to obtain the variational form for the elliptic saddle point equations of motion and continuity and an SUPG formulation is used to obtain the variational form for the hyperbolic constitutive equation. This is a very robust method that works well for a wide range of Capillary (*Ca*), Weissenberg (*Wi*) and Gravity (*Gr*) numbers. Our study indicates the presence of two distinct flow regimes. A recirculation flow at low *Ca* numbers and a bypass flow at high *Ca* numbers. For the recirculation flow, our study reveals the formation of elastic stress boundary layers in the capillary transition region, the thickness of which decreases with *Wi* number, an increase in the hydrodynamic film thickness with increasing elasticity and a meniscus invasion when the boundary stresses get large enough. We also illustrate how the elastic stress boundary layers can be modeled using a birefringent strand formulation. For the bypass flow, the stress profiles are qualitatively different. We have also studied the effect of gravity on both flows. We discuss how both flows are elastically unstable and plausible mechanisms for the onset of instability are suggested.

Tuesday 10:35 Grand Station III VF17

Modeling free boundary flows in wire coating and pipe extrusion

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Mechanical Engineering, University of Wisconsin - Madison, Madison, WI 53706

In wire coating, polymer melt is extruded through an annular die and then drawn onto a wire, with a vacuum applied to the inner annular surface. In pipe extrusion, the annular extrudate is pressed into a sizing sleeve, sometimes using a positive pressure applied to the inner annular surface. For both flows, there is an annular free boundary flow between the die and a radial constraint. The similarity between these two flows suggests that these could be modeled similarly. These flows also resemble tubular film blowing, for which solutions exist. Here, the available literature on wire coating and pipe extrusion is reviewed. Analytic and numerical models are developed for these flows. These models include solutions for non-Newtonian fluids, specifcally power-law and upper convected Maxwell fluids. Solutions are presented in ways most helpful to practitioners saddled with designing process equipment and predicting operating parameters.

Tuesday 11:00 Grand Station III VF18

Molecular architecture controls misting in roll coating

Michael S. Owens, Christopher W. Macosko, and L. E. Scriven
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Misting is the generation of airborne liquid droplets (less than 50 microns in diameter) in the splitting of a liquid film carried through the nip or gap between two rolls of a smooth roll coater or printing press. When coating low viscosity Newtonian liquids at high roll speeds mist is generated. To reduce mist, high molecular weight polymers are added to otherwise Newtonian solutions, but characterization of their rheology has not been possible until recently. High speed cameras, a filament thinning rheometer, and a time-of-flight mist analysis technique were used to understand how misting mechanisms, droplet size and number are influenced by solution rheology and molecular architecture.

Low viscosity (50-500 mPa-s) Newtonian liquids breakup into mist droplets by the rupturing of webbed liquid sheets extend from the coating nip called septa. As roll velocity and viscosity were raised the number and size of droplets increased. Increasing surface tension, which stabilizes septa, lowered the number of mist droplets while droplets size remained constant. Mist levels can be reduced further by addition of high-molecular weight polymers.

Low viscosity polymer solutions generate mist by failure of filaments stabilized by viscoelasticity, but simply measuring viscoelasticity of these solutions is difficult due to inadequate transducer sensitivity and inertia. These limitations were overcome by using a capillary thinning rheometer. Characterizing the extensional rheology and misting behavior of PDMS and PEO solutions was accomplished using a capillary thinning rheometer in combination with a time-of-flight drop analysis. We observed the number of mist droplets falls while droplet size rises with addition of low levels (5-500 ppm) of linear and branched polymers. Solution relaxation times were correlated to the number and size of droplets, and comparisons of branched and linear polymer solutions were made.

Tuesday 11:25 Grand Station III VF19

Flow instabilities near soft elastic solids: linear and nonlinear behavior

Vasileios Gkanis, Matthew Eggert, and Satish Kumar

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

Fluid flows near soft elastic solids are prone to instabilities that bear many resemblances to those encountered in viscoelastic fluid mechanics. In addition to being of potential importance for practical applications such as membrane separations, microfludics, and bio-physics/engineering, study of such instabilities may also shed light on the behavior of fluids that undergo flow-induced gelation. In order to understand the role that nonlinear rheological properties of the solid play in these elastohydrodynamic instabilities, we apply linear stability analysis to investigate creeping Couette flow of a Newtonian fluid past an incompressible and impermeable neo-Hookean solid of finite thickness. Experiments in a parallel-plate rheometer with PDMS gels and a viscous Newtonian liquid shed light on instability behavior in the nonlinear regime. With the neo-Hookean model, there is a first normal stress difference in the base state that gives rise to a shortwave instability which is not present if a linear elastic model is used. Instability behavior is explored over a wide range of the problem parameter space, and mechanisms are uncovered through analysis of the kinematic boundary condition. In the experiments, the stress is increased at a constant rate, and an increase in the apparent viscosity is observed above a critical stress. If the stress is then decreased, the apparent viscosity exhibits hysteresis, whereas if the stress is held constant (above a critical value), the apparent viscosity exhibits sustained oscillations.

Symposium EA
Entangled Polymers and Analytical Rheology

Organizers: Monty Shaw and James P. Oberhauser

Tuesday 9:45 Grand Station IV EA1

Dielectric and viscoelastic behavior of polyisoprene blends: Test of tube dilation mechanism

Hiroshi Watanabe and Satoshi Ishida

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Dielectric and viscoelastic measurements were conducted for entangled binary blends composed of cis-polyisoprenes (PI) having type-A dipoles to test the molecular picture of dynamic tube dilation (DTD). The component PIs had widely separated molecular weights M. If the DTD picture is valid, the viscoelastic relaxation function $G(t)$ of the blend can be expressed as a power of the survival fraction of the dilated tube $f(t)$ with the power-law exponent of $p = 2\text{-}2.3$, and the dielectric relaxation function $F(t)$ of the type-A PI is essentially equivalent to $f(t)$ (except a minor correction for the fluctuation at the dilated tube edge). For blends containing concentrated (mutually well entangled) high-M PI chains, this DTD relationship between $G(t)$ and $F(t)$ was found to be valid at short and long times (where the low-M and high-M chains exhibited respective terminal relaxation), and the DTD exponent p was close to 2.2. However, in an intermediate time scale, the DTD relationship was found to fail. This result suggests that the mutual equilibration of the entanglement segments of the high-M chain occurring through the constraint release (CR) process is not fast enough compared to that time scale. Thus, the CR mechanism plays a fundamental role in the relaxation at intermediate *t*.

Tuesday 10:10 Grand Station IV EA2

Constitutive transition in strong flow of entangled polymeric fluids

Prashant Tapadia and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH

We report a recent discovery [1] of unexpected constitutive behavior in entangled polymer solutions. At and beyond a critical stress, the initially uniform and well-entangled sample transforms from its entangled (coiled) state into a fully disentangled (stretched) state over a period, during which the resulting shear rate, normal stress and optical retardation all increase sharply over orders of magnitude. Hysteresis behavior is also observed. The same sample behaves differently in the mode of controlled shear rate where in contrast all shear rates are accessible and a stress plateau shows up over three decades of shear rate. The detailed features of this remarkable and generic phenomenon will be presented in terms of both rheological and rheo-optical measurements.

[1] P. Tapadia and S. Q. Wang, “Constitutive Transition in Entangled Polymeric Fluids”, Phys. Rev. Lett., submitted on April 25th, 2003.

Tuesday 10:35 Grand Station IV EA3

Stress relaxation measurement following step strains in entangled linear polymer liquids

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The desire to understand the flow behavior of entangled linear polymers with narrow molecular weight distribution has attracted the attention of experimental and theoretical rheologists for many years. The most successful theoretical model to date for such systems is the tube model of de Gennes developed into a constitutive model by Doi and Edwards. One of the most widely studied rheological flows is stress relaxation following a step shear s from which the shear modulus $G(s,t)$ can be obtained. For many polymer liquids it is observed that for times greater than some characteristic time, the ratio $G(s,t)/ G(t)$, where $G(t) = G(s,t)$ for $s << 1$, is independent of time. When this behavior, often referred to as time-strain factorability, is observed it is common to introduce the damping function: $h(s) = G(s,t)/ G(t)$. The tube model predicts time-strain factorability for times greater than a characteristic time and its prediction for the damping function has been found to be in good agreement with experimental data on a large number of linear, mono-disperse polymer liquids. There are, however, a significant number of cases where tube model predictions are qualitatively different from experimental stress relaxation data. Even more troubling is the fact that these differences are observed for very highly entangled polymers, where one would expect the tube model to be most applicable. It has been argued by some authors that discrepancies between experiments and tube model predictions are the result of shortcomings of the theory, while others argue that slip, either true or apparent, is the cause. In this study, we carefully examine published step strain data and attempt to establish if slip, or some other phenomena, can explain experimental data from step strain flows that are inconsistent with tube model predictions.

Tuesday 11:00 Grand Station IV EA4

A reptation model without an excluded volume constraint

Fang Xu[1], Morton M. Denn[1], and Jay D. Schieber[2]
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The full-chain reptation model of Hua and Schieber [1 - 3], which incorporates chain/ tube interactions, segment connectivity, chain-length breathing, segment stretch, and constraint release in a one-dimensional stochastic algorithm, includes an excluded volume constraint that prevents chain loops from forming and collapse of the chain within the tube. We describe here the effect of removing the excluded volume constraint and adding a self-consistent effective chain tension that prevents collapse in the tube and preserves the proper equilibrium chain length. Shear thinning at high rates is increased by removal of the excluded volume constraint but decreased by the effective chain tension. The magnitude of the stress at a given shear rate is dependent on the number of free links in the chain because of the one-dimensional projection inherent in the model. The behavior of the model is qualitatively the same with and without excluded volume.

1. Hua,C. C., and Schieber, J.D. Segment connectivity, chain-length breathing, segment stretch, and constraint release in reptation models. I. Theory and single-step strain predictions, J. Chem. Phys., 1998, 109:10018
2. Hua,C. C., Schieber, J.D., and Venerus, D. C. Segment connectivity, chain-length breathing, segment stretch, and constraint release in reptation models. II. Double-step strain predictions, J. Chem. Phys., 1998, 109:10028
3. Hua,C. C., Schieber, J.D., and Venerus, D. C. Segment connectivity, chain-length breathing, segment stretch, and constraint release in reptation models. III. Shear flows, J. Rheol. 1999, 43:701

Tuesday 11:25 Grand Station IV EA5

A rigorous approach to the dynamics of entangled polymer melts

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A rigorous theoretical description of the dynamics of entangled polymer melts within the framework of the tube model is presented. The description is centered around the Bond Vector Probability Distribution Function (BVPDF) $f(\mathbf{b},s,t)$. The bond vector $\mathbf{b}(s,t)$, i.e. the vector tangent to a polymer chain (as represented by a space curve) at position s along the chain and at time t, describes the local chain orientation via its direction and the local chain stretching via its length. All macroscopic quantities of practical interest pertaining to the melt, e.g. the stress tensor, can be expressed via second order moments of this BVPDF. We derive a time evolution equation for this BVPDF taking into account all major relaxation mechanisms such as contour length fluctuations, reptation and (convective) constraint release. The resulting equation is quite universal. For instance it is valid for all flow regimes. Furthermore, the description is not limited to bulk melts. It is also shown that melts interacting with solid walls containing tethered chains can be described within the same framework with only minor modifications. We also discuss how this rigorous approach relates to earlier theories such as the original Doi-Edwards model, the DEMG model by Marrucci et al. and the Contour Variable model of Mead, Larson and Doi.

Symposium MM
Microrheology, Microfluids and MEMS

Organizers: Gerry Fuller and Kalman Migler

Tuesday 9:45 Grand Station V MM15

Shear and extensional microrheometry of protein solutions and other complex biofluids

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We describe the design and construction of two new microrheometers designed to facilitate the study of complex fluids using very small sample volumes (1-10 μl). The shear-rate-dependent viscosity is measured using a sliding plate microrheometer with optical flats (polished flat to within 30nm) as the shearing surfaces. White light interferometry and a three-point nanopositioning stage employing piezo-stepping motors are used to control the parallelism of the upper and lower surfaces. A compound flexure system is used to hold the fluid sample between a drive spring and an independent sensor spring. Alignment fidelity and device orthogonality are minimized by machining the entire instrument frame from a single monolithic aluminum block using water-jet and EDM technology. Displacements in the sensing flexure are detected using an inductive proximity sensor with a resolution of 3 nm allowing the detection of loads up to 6 N with an accuracy of 3 mN. The lower plate is driven by an 'inchworm' motor with a resolution of 0.1 nm and a maximum displacement of 6 mm, thus allowing large strains to be obtained. The transient extensional rheology is also measured using a 1 μl fluid droplet in a microscale capillary

break-up extensional rheometer. The extensional flow is driven by capillarity and resisted by the viscous and elastic stresses in the elongating fluid thread.

These devices are used to quantify the rheological properties of the spinning dope extracted ex vivo from the major ampullate gland of a Nephila clavipes spider. The present study shows that the shear viscosity of this 30wt% protein solution decreases ten-fold as it is pushed through the long narrow converging S-duct in the abdominal cavity of the spider, whereas the extensional viscosity increases more than one hundred-fold during the spinning process. Quantifying the properties of native spinning solutions provides new guidance for adjusting the spinning processes of synthetic or genetically-engineered silks to match those of the spider

Tuesday 10:10 Grand Station V MM16

DNA dynamics in a microchannel: Confinement, hydrodynamic interactions and shear-induced migration

Richard M. Jendrejack[1], Juan J. de Pablo[2], and Michael D. Graham[2]
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We simulate dilute solution dynamics of long DNA molecules (O(10-100) microns) in pressure-driven flow through micron-scale channels, using a self-consistent coarse-grained Langevin description of the polymer dynamics and a numerical solution of the flow generated by the motion of polymer segments. During flow, the chains migrate toward the channel centerline in agreement with well-known experimental observations. The thickness of the resulting hydrodynamic depletion layer increases with molecular weight at constant flow strength; higher molecular weight chains therefore move with a higher average axial velocity than lower molecular weight chains. In contrast, when the hydrodynamic effects of the confining geometry are neglected, depletion of concentration is observed in the center of the channel rather than at the walls, contradicting experimental observations. The mechanisms for migration are illustrated using a simple kinetic theory dumbbell model of a confined flexible polymer. The simple theory correctly predicts the trends observed in the detailed simulations. We also examine the steady-state stretch of DNA chains as a function of channel width and flow strength. The flow strength needed to stretch a highly confined chain away from its equilibrium length is shown to increase with decreasing channel width, independent of molecular weight; this is fairly well-explained using a simple blob picture.

Tuesday 10:35 Grand Station V MM17

Flow-induced interfacial nanostructures by dip coating micellar solutions

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Thin films with self-assembled nanostructures are important in applications such as catalysis, synthesis, and biosensor technology. A major technique used to prepare such films is sol-gel processing. This technique involves depositing a complex fluid containing colloids, alcohol, and surfactants on a substrate by coating, followed by allowing the film to evaporate and form self-assembled nanostructures. The fundamental mechanisms underlying this process are poorly understood. Here, we present a program designed to explore the formation of self-assembled nanotructures with respect to dip coating. By varying the components and concentration of the coating fluids and coating speed, we measure the steady-state film thickness and characterize the final mesostructure of the dried porous film. We show that the self-assembled nanostructure is highly dependent on the coating dynamics (chemically- and thermally-induced Marangoni effects), the rheology of the fluids, and micellar kinetics. This systematic study will offer a unique perspective on self-assembled nanostructures based on rheology and coating dynamics, which will broaden the existing knowledge in synthesis of nanostructured materials.

Tuesday 11:00 Grand Station V MM18

Dynamics of single polymer collisions in microfluidic devices

Greg C. Randall and Patrick Doyle
Chemical Engineering, MIT, Cambridge, MA

When a polymer molecule is driven into a stationary obstacle, a wide variety of molecular dynamics are observed. Some molecules merely roll-off, while others form asymmetric J-shaped hooks that disengage like a rope-on-a-pulley, while still others form symmetric U-shaped hooks whose disengagement is driven by thermal fluctuations. We present a comprehensive study of a single DNA molecule in electrophoretic motion colliding with a

microfabricated obstacle. In this investigation, we postulate physical models that describe the full "phase-diagram" of collision events. These models are supported by single DNA molecule fluorescence microscopy experimental data. The models and data supplement work to create an improved DNA separation device for large DNA molecules (> 48.5 kbp) in which the separation mechanism is the collision of the DNA with a stationary obstacle. These single molecule studies reveal the dependency of the collision time distribution on electric field strength, DNA size and obstacle morphology. Furthermore, they provide insight into the “molecular individualism” of polymer collisions.

Tuesday 11:25 Grand Station V MM19

Single molecule visualization of DNA in pressure-driven flow in a rectangular microchannel

Connie K. Smith, Rajat Duggal, and Matteo Pasquali
Chemical Engineering, Rice University, Houston, TX 77005

Understanding the individual dynamics of flowing polymer molecules will further our control of many important processes, from synthetic polymer coatings and ink-jet printing to microfluidics and DNA arrays. Direct visualization of single molecule dynamics has been limited by the small size of synthetic polymers. Biopolymers such as DNA are now used to study single molecule dynamics in flow due to their larger size and monodispersity. We study the dynamics of DNA molecules in dilute solution in a pressure-driven channel flow. Our apparatus consists of a rectangular channel that has been plasma ion etched into a silicon wafer with the flow driven by a pulse-free syringe pump. The dynamics of the DNA molecules in flow are monitored using fluorescence microscopy and digital image acquisition and analysis. The flow channel was designed to allow for visualization of the molecules in the plane defined by velocity and velocity gradient instead of the plane identified by the velocity and the vorticity as previously studied by Smith et al (1999) and LeDuc et al (1999). Moreover, the DNA experiences a flow with non-uniform velocity gradient. The individual and average conformations (size and orientation) of the flowing DNA molecules are being studied as a function of the Weissenberg number (*Wi*, product of strain rate and DNA relaxation time), which is based on the individual molecule's distance from the channel walls. In agreement with the previous works in homogeneous shear flow (Smith et al 1999, Hur et al 2000), we find a non-linear increase in molecular extension with increasing *Wi* which asymptotes to less than 50% of the contour length.

Tuesday Afternoon

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Tuesday 1:30 Grand Station I SM20

Effect of compatibilization on the deformation and breakup of droplets in polymer blends

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Block copolymers are often used as compatibilizers during polymer processing to facilitate blending of immiscible polymers. The addition of a compatibilizer has consequences for the morphology of the polymer blend. In the case of a droplet/matrix structure the mean droplet size of the dispersed phase is reduced. One reason for this reduced size is the decrease of the interfacial tension, which facilitates breakup of droplets. However, this is not the only effect of compatibilization. Phenomena such as coalescence suppression and interfacial viscoelasticity have also been noted in compatibilized polymer blends. Here, the deformation and breakup of droplets in compatibilized blends of polyisoprene (PI) and polydimethylsiloxane (PDMS) will be studied, both by rheology and light scattering experiments. The compatibilizers used in this work are model diblock copolymers of PI and PDMS, which were synthesized at the university of Minnesota, Minneapolis. A particular shear history has been used, consisting of preshearing at a low shear rate to ensure a well-defined initial morphology after which the shear rate is suddenly increased. During flow, both the evolution of shear and normal stresses has been monitored as well as the evolution of the small angle light scattering patterns. It is known that droplets in uncompatibilized blends are deformed and finally broken up by the applied shear forces. For blends containing small amounts of compatibilizer, droplets are still deformed and broken up by the flow but a clear effect of compatibilizer concentration on breakup times is observed. For blends containing a high concentration of block copolymer and under appropriate flow conditions, the droplets are no longer deformed and do not break anymore, a change that can be detected rheologically and with light scattering.

Tuesday 1:55 Grand Station I SM21

Drop breakup in shear flow

Vittorio Cristini
Biomedical Engineering, University of California, Irvine, Irvine, CA

We report a study on the deformation and breakup of viscous drops in an impulsively-started shear flow. We used adaptive boundary-integral simulations and video-microscopy experiments. We find that the size of droplets produced by breakup events scales with the maximum stable drop size in the flow, and the parent drop volume determines the number, but not the size, of droplets produced. The drop size distribution resulting from breakup events in a dilute sheared emulsion is roughly tri-modal, with one drop size largely dominant, and is independent of the poly-dispersity of the emulsion before shear is applied. We also demonstrate the existence of an optimal shear rate corresponding to minimum breakup time.

Tuesday 2:20 Grand Station I SM22

A new mechanism for drop breakup in emulsions under shear

Xinyu F. Zhao and Jacqueline L. Goveas
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High-speed video microscopy is used to study the deformation and breakup of Newtonian drops suspended in another Newtonian liquid under shear, particularly at high shear rates. Effects of capillary number (viscous stress *vs.* capillary pressure) and viscosity ratio (inner phase viscosity *vs.* outer phase viscosity) on the breakup-mode, the thread width at breakup, the wavelength, and the final drop sizes are investigated.

The dominant mechanism of drop breakup at high shear rates is capillary instability. The instability is suppressed until the thread reaches a pseudo-steady state with a certain critical width, which is independent of the initial drop sizes. We define a dimensionless thread number, $T = \mu \dot{\gamma} R_b / \sigma$, where μ is the outer phase viscosity, $\dot{\gamma}$ is the shear rate, R_b is thread radius at breakup, and σ is the interfacial tension. This thread number is a constant at a fixed viscosity ratio. This work provides the first experimental evidence verifying a theory due to Hinch and Acrivos [J. Fluid Mech., 1980].

For viscosity ratios between 0.1 and 1, size selection of the thread width at breakup and the wavelength leads to monodisperse dilute emulsions. By contrast, at viscosity ratios lower than 0.1, the daughter drops formed by the capillary instability further elongate and collide into each other leading to drop re-breaking and coalescence. This re-breaking and coalescence mechanism results in polydisperse drops. The collision occurs at capillary numbers above a certain value, and this value decrease as viscosity ratio decreases.

Tuesday 2:45 Grand Station I SM23

Modeling coalescence, breakup and relaxation of polymer droplets

Anne A. Leyrat[1], Matthieu Brizard[1], Claude Verdier[1], Thierry Biben[2], and Chaouqi Misbah[2]
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The interactions of polymer droplets are investigated both experimentally and theoretically. First we consider the influence of the viscosity ratio in the dynamics of Newtonian fluid droplets [1] and we exhibit PIV measurements carried out inside and outside droplets during coalescence [2]. This enables us to have access both to the shape of the interfaces but also to velocity fields.

It is then possible to compare such results with numerical predictions. We use the method of the advected field [3] which is adapted to study the dynamics of fluid interfaces [4]. Quantitative predictions of the stability of droplets under shear and elongational flows are provided. We also look at the relaxation of droplets after elongation and find good agreement with the data of Ha and Leal [5]. Finally comparisons are shown for the coalescence of polymer droplets.

The method [3] is general enough so that it can be extended to non-Newtonian systems.

[1] Verdier C, The influence of the viscosity ratio on polymer droplet collision in quiescent blends, Polymer, 42(16), 6999-7007 (2001)
[2] Verdier C, Brizard M, Understanding droplet coalescence and its use to measure interfacial tension, Rheol. Acta, 41, 514-523 (2002)
[3] Biben T, Misbah C, An advected-field method for deformable entities under flow, Eur. Phys. J. B, 29, 311-316 (2002)
[4] Biben T, Misbah C, Leyrat A, Verdier C, An advected-field approach to the dynamics of fluid interfaces, submitted to Europhys. Letters (2003)
[5] Ha J-W, Leal LG, An experimental study of drop deformation and breakup in extensional flow at high capillary number, Phys. Fluids, 13, 1568-1576 (2001)

Tuesday 3:35 Grand Station I SM24

Large scale hydrodynamic simulations of emulsions and foams

Jonathan L. Higdon and Malcolm S. Talbot
Chemical Engineering, University of Illinois, Urbana, IL 61801

Large scale hydrodynamic simulations are presented for two dimensional sheared suspensions of viscous droplets. Systems with up to 400 droplets are studied using an N ln N boundary integral formulation. A range of volume fractions is considered from dilute systems through 95% dispersed phase area fraction. A range of capillary numbers is considered for droplets with viscosity ratios of 0.1, 1, 10.

Results for perfectly ordered systems show the minimum viscosity with interesting non-monotonic behavior (as a function of volume fraction) for low viscosity droplets. Transitions from rolling/sliding motion to rapid deformation are shown to be responsible for this behavior. Simulations for large scale systems (100 droplets through 400 droplets) exhibit disorder-order transitions at area fractions greater than approximately 70% dispersed phase. The exact transition point is a function of viscosity ratio and capillary number. As system size is increased from 100 to 400 droplets, the additional degrees of freedom allow the appearance of non-homogeneous deformation zones including shear bands and localized non-deforming fluid regions. Simulations for viscosity ratio of 1 exhibit multiple time periodic asymptotic states with different viscosities depending on the initial conditions. Disordered systems exhibit higher suspension viscosity compared to perfectly ordered systems for all viscosity ratios. Time average suspension viscosities above the disorder-order transition point closely approach those for the perfectly ordered system.

Tuesday 4:00 Grand Station I SM25

A constitutive equation for highly viscous foam

Masao Doi[1] and Andrew M. Kraynik[2]
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Seven decades ago Derjaguin (Kolloid-Z 64, 1933) derived a simple microstructural theory for the shear modulus of foam by assuming affine deformation of randomly oriented films. Remarkably, this highly idealized view of foam structure and microrheology over-predicts the shear modulus of dry soap froth by less than a factor of two. The linear theory developed by Derjaguin applies to zero capillary number. We have developed a nonlinear microstructural theory for the rheology of highly viscous foam. The primary contribution to the foam stress comes from viscous flow in thin liquid films. In the spirit of Derjaguin, we assume that the midplane of randomly oriented films undergoes affine deformation. Results for Newtonian continuous phase are presented.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract #DE-AC04-94AL85000.

Tuesday 4:25 Grand Station I SM26

Rheological study of injection-molded LDPE foams

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A low-density polyethylene (LDPE) was selected to make polymeric foams with an injection-molding machine by dry mixing the LDPE with a chemical blowing agent. First, the decomposition behavior of the chemical blowing agent was studied by thermogravimetric analyzer (TGA). Then the LDPE containing the chemical blowing agent was processed in injection molding at high injection speed to make cellular foams. Most bubbles were found to be closed in the final foam product. Typical cell diameters were of 41mm and 30mm in volume and number average, respectively and a cell density up to 6.88×10^6/mL (pure polymer) was obtained. The linear viscoelastic properties of LDPE and injection molded LDPE foams have been investigated using a controlled stress rheometer with a concentric disk geometry. The measurements were carried out under nitrogen in the linear regime at a set temperature of 120°C. This selection of temperature was considered from thermal stability of the foams. The effect of different bubble volume fractions in foams was also studied. For all bubble volume fractions, both the loss modulus and storage modulus of the foams were found to be significantly smaller than the moduli of the LDPE and decrease with the volume fraction. The Palierne model (1) was used to fit and predict the linear behavior of the polymeric foams. An excellent agreement between the experimental data of small amplitude oscillatory tests and the theoretical predictions was obtained for different bubble volume fractions. The bubble volume fractions used in the calculations were obtained from the density measurements of the foams and LDPE. The effects of the cell morphology and of the interfacial tension between the bubbles were assumed to be negligible. In other words, the linear viscoelastic properties of LDPE foams depend only on the linear viscoelastic properties of the LDPE and on the volume fraction of the bubbles.

1. Palierne, J.F., Rheol. Acta, 29, 204 (1990)

Tuesday 4:50 Grand Station I SM27

Stability of "solid-stabilized" emulsions

Gerald G. Fuller and Edward Stancik
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Colloidal particles are often used to stabilize emulsions, and offer particular advantages compared with the use of surfactants. For example, by controlling the preferential affinity of particles to either an oil or aqueous phase, one can stabilize either oil-in-water or water-in-oil emulsions. These systems have also been observed to have longer "shelf lives" than systems stabilized with molecular amphiphiles. In this paper, model interfaces are examined for their interfacial rheology and drainage characteristics. For this purpose, mono-sized polystyrene spheres with diameters in the range of 1 to 5 microns were placed at the interface between water and decane. These spheres self assemble into two-dimensional crystals that strongly enhance the surface viscoelasticity of the interface. The dynamic moduli of these 2D suspensions were measured using an "interfacial stress rheometer" (ISR) and a "time-concentration" scaling was found to collapse the data acquired over several orders of magnitude. The appearance of the scaled data is remarkably similar to data reported on bulk dispersions of weakly attractive particles. The drainage characteristics of these interfaces were studied by monitoring the approach of two particle-laden interfaces using optical microscopy. This was accomplished by bringing a droplet of decane covered with particles towards a flat, decane/water interface that contained the same particles. The resulting images reveal a complex sequence of events as the two crystalline layers interact and finally merge.

Symposium VF
Viscoelastic Flows and Instabilities

Organizers: Jonathan Rothstein and Bamin Khomami

Tuesday 1:30 Grand Station III VF20

Modeling of fast contraction flows of polymers

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This work develops isothermal and non-isothermal models, with no adjustable parameters, for fast (high Deborah number) contraction flows of polymers from a reservoir to a die of circular or rectangular cross-sections. Two components of composite flow models in different regions of the flow domain are connected in succession with the use of asymptotic matching boundary conditions. These components are inhomogeneous elongation and a modified unsteady shearing. Although calculations in the present model are based on viscoelastic constitutive equations elaborated in our research group, any constitutive models suitable for polymers could be used. The model employs easy PC numerical calculations, and demonstrates a reasonable good agreement with available experimental or direct numerical data. This agreement is improved when the flow Deborah number and/or contraction ratio are increasing. Using the model, we also analyzed the extrudate swell in flows of polymer fluids in short capillaries.

Tuesday 1:55 Grand Station III VF21

Modeling and simulation of polymer degradation in contraction flow

Israel B. Owusu and Yong L. Joo
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The polymer chains may fracture in flows fields if the deformation rate is sufficiently high. Such degradation is often undesirable because it will alter the flow behavior and thus the processing characteristics and eventually affect the final product. In the turbulent drag reduction study, for example, polymer degradation is an important phenomenon that plagues most attempts to implement polymer additives in aqueous environments. On the other hand, degradation in flow fields can be used to fragment DNA chains for sequencing and cloning purposes or to prepare monodisperse polymers from polydisperse ones. The goal of this study is to understand fragmentation dynamics of macromolecules in complex flows where both shear and elongational components are important. Using input from stochastic simulations of multi-bead rod models, we wish to develop a simple coarse-grained model which describes scission dynamics. The new model is then used in complex flow simulation of polymers in dilute solutions. We first develop a constitutive model in which degradation dynamics is captured in an additional evolution equation for the maximum length of the segment. The segment is modeled as either FENE chain for synthetic, flexible polymers or wormlike chain for DNA molecules. We examine the flow behavior of these molecules in contraction flows with the new model. Our simulation results show that a higher contraction ratio results in a narrower distribution of fragmented chain lengths. Predictions for both synthetic, flexible polymers and DNA molecules are compared with experiments.

Tuesday 2:20 Grand Station III VF22

Parallel shear flow of a fluid with pressure dependent viscosity

Michael Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

We investigate the existence of pressure driven parallel shear flow of a Newtonian liquid with a pressure dependent viscosity. In general, such flows exist if the dependence of viscosity on pressure is linear, and in the case of planar flow, this is the only case for which a parallel flow exists. Surprisingly, however, there are other cases which are possible in axisymmetric flow. We show that there are exactly three possible cases: The case of linear dependence of viscosity on pressure, a solution found by Denn in 1981 for which the velocity profile is quadratic and the viscosity depends exponentially on pressure, and a third possibility for which the velocity depends linearly on the radius (this third solution has a singularity at $r = 0$ but is possible in an annulus).

Tuesday 2:45 Grand Station III VF23

Characterization and control of sharkskin instability through localized thermal modification

Erik Miller and Jonathan P. Rothstein
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At wall shear stress levels on the order of 0.1 MPa, most extruded polymers exhibit a surface instability commonly referred to as sharkskin. This instability is typically unacceptable for commercial applications and has motivated a great deal of research to characterize the nature of the instability and delay its onset to higher stress levels and subsequently increased output rates. We will present experimental work that was performed using a custom fabricated extruder and series of special dies incorporating thermal breaks that allowed for precise localized heating and cooling of the extrudate. This configuration was used to induce temperature profiles across the extrudate, which compare well with numerical simulations. We will present data correlating the amplitude and frequency of the sharkskin to bulk and die surface temperature as well as stress levels. The results show that the instability can be suppressed or controlled by isolated heating or cooling of the extrudate as it exits the die. We will also show that the relatively low thermal conductivity of polymers makes it possible for this local heating to control the surface instability by causing a stratification of the rheological properties of the extrudate. By allowing the bulk fluid temperature to remain cool, this technique minimizes the cost of heating and the time for cooling in a commercial extrusion process. Furthermore, by altering only temperature of extrudate near the surface, our research supports the hypothesis that sharkskin originates not in the bulk, but at the stress singularity present at the die exit. Finally, we

will discuss using this technique to precisely control sharkskin for designing specific desired functionality into extruded surfaces.

Tuesday 3:35 Grand Station III VF24

Constitutive origin of sharkskin-like melt fracture: An update

Zhiyong Zhu and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH

Sharkskin like melt fracture in polymer extrusion has been a well-known and well-studied phenomenon. There has been some debate about the mechanisms for sharkskin: One correlated the occurrence of sharkskin below the global stick-slip transition to exist slip flow; the other recognized the importance of extensional flow component in the exist region that may cause rupture of the surface layer of the extruded melt. All proposals for the correct mechanism face the challenge of explaining why the surface roughness is quasi-periodic and why its magnitude diminishes as the level of chain entanglement decreases. So far the search for any wall slip inside the die has turned out negative as multiple observations will show, contradicting the interfacial stick-slip oscillation mechanism previously inferred from the apparent relationship between where sharkskin occurs and where an overall stick-slip transition takes place. The surface rupture mechanism also suffers from the uncertainty of whether the perceived extensional flow is the effect or the cause for sharkskin. Inspired by the recent discovery of a constitutive transition for entangled polymers from the entangled state to the disentangled state, we reexamine this difficult problem and suggest the possibility that the origin of sharkskin is constitutive in absence of any evidence for wall slip within the die exit and that the cause arises from the exiting material suffering from its constitutive transition to the state of disentanglement, which is not sustainable, resulting in the periodic repetition of the cycle. Phenomenologically, the cycle involves development of a fast flowing layer (in the disentanglement state) to ensure the no-slip boundary at the exit and disappearance of the fast flowing layer away from the exit along with its redevelopment at the exit, which initially amounts to an appreciable surface velocity at the exit and gives the impression of plug-like flow upon exiting the die.

Tuesday 4:00 Grand Station III VF25

The gas-assisted full slip extrusion of molten polyethylene

Ruifeng Liang[1] and Malcolm R. Mackley[2]
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Although gas injection is a well-developed technology in the field of injection molding where in particular hollow moldings are produced with better surface quality, however, it does not appear that gas injection has been used for polymer extrusion. Extrusion production rates are usually limited at a certain level above which the polymer melt flow becomes unsteady and the sharkskin occurs on the extrudate surface. Many published researches support the conclusion that polymer extrudate such as PE extrudate surface defects originate from the die wall or exit zone and can be affected by the material of construction of the die and that these defects may be reduced or eliminated by promotion of the wall slip, either by using a fluoropolymer additive, or by use of a slippery surface such as PTFE. In this work, polyethylene was extruded by a novel gas-assisted extrusion process where gas (nitrogen) was injected from a narrow slit at the metal die /polymer melt interface at a low flow rate to establish a stable downstream gas layer for both a slit and rod geometry. Both the experiments and Polyflow simulation demonstrate that the gas layer had a profound effect on the process rheology of the flowing melt by providing a full slip downstream boundary condition. Typically, the modifications with gas injection included faster downstream stress relaxation, a significant reduction in pressure difference and substantially reduced die swell. These modifications offer at least two distinctive advantages over conventional extrusion, i.e. near elimination of die swell and a near stress free extrudate. However, the results indicate that gas-assisted extrusion offers no improvement in the onset of sharkskin. The gas injection just moves the stress concentration upstream from the normal exit to the gas injection point.

Tuesday 4:25 Grand Station III VF26

Negative wake and velocity discontinuity of a bubble rising in a viscoelastic fluid

Shriram Pillapakkam and Pushpendra Singh
Department of Mechanical Engineering, New Jersey Institute of Technology, Newark, NJ

A three-dimensional finite element based numerical method is used to simulate the rise of a bubble in viscoelastic fluid modeled by the Oldroyd-B model. The rise velocity is studied as a function of bubble volume on a log-log plot and the dependence of rise velocity on the viscoelastic properties of the ambient fluid are also investigated. In simulations, rather than a jump in rise velocity at critical volume as observed in experiments, we find that there is a steep, but continuous increase in rise velocity over a very small range of bubble volumes. Interestingly this steep increase in rise velocity is exaggerated when a parameter, which is a measure of polymer concentration, is increased while keeping the zero-shear viscosity a fixed. The wake of a bubble rising in a viscoelastic fluid is 'negative' in the sense that the direction of fluid velocity behind the bubble for a certain parameter range is the opposite of that observed for a bubble rising in Newtonian fluid. The existence of negative wake, the magnitude of maximum negative velocity and the position of recirculation zone behind the trailing edge of the bubble are explored as a function of viscoelastic properties of the ambient fluid.

Tuesday 4:50 Grand Station III VF27

The influence of elasticity on the drop formation and spraying processes

Heather Shore, Gyo Park, and Graham M. Harrison
Chemical Engineering, Clemson University, Clemson, SC 29634

The presence of small amounts of polymer in Newtonian solvents can have a significant impact on the flow behavior of these fluids in extension-dominated flows. This study investigates the effect of elasticity on the drop formation and the spray atomization processes through the use of low viscosity elastic liquids. A high speed camera is employed to observe drops ejected from a nozzle using a piezoelectric sleeve. We observe that an increase in polymer concentration or molecular weight leads to a suppression of the satellite drops common with Newtonian fluids of identical shear viscosity. However, the resultant increased elasticity in the solution requires a greater pulse strength to eject the drop. The criteria necessary to eliminate the satellite drop formed from the drop thread are identified. The spraying of low viscosity elastic liquids is also probed. We study how increased elasticity narrows the drop size distribution by employing a drop size analyzer also capable of measuring the instantaneous velocity of the drops in the field of view. The drop size distribution throughout the spray is investigated as a function of the geometry of the nozzle and the fluid properties. In addition, the effects of elasticity on the velocity distribution of drops throughout the spray region are quantified.

Symposium EA
Entangled Polymers and Analytical Rheology

Organizers: Monty Shaw and James P. Oberhauser

Tuesday 1:30 Grand Station IV EA6

A sliplink model with self consistent constraint release

Jay D. Schieber and Deepa Nair
Chemical Engineering, Illinois Institute of Technology, Chicago, IL

We introduce a temporary network model for describing the stresses in entangled polymers. Unlike traditional network models, chains are allowed to slide through the entanglements, as in the sliplink picture of Doi and Edwards. Also, the creation and destruction of entanglements is not postulated a priori, but rather follow from the dynamics of the chain. When an entanglement is abandoned by a chain, it dies, and new entanglements are created only at the ends of the chains. Since information about the full chain is present in the model, it exhibits contour length fluctuations, chain stretching, and segment connectivity in a rigorous way. Inspired by the ideas of Rubenstein and Colby, we also introduce constraint release. The entanglements are postulated to move in Rouse dynamics, with time scales determined by the reptation-like dynamics. These constraint release dynamics are still mean field, but now found in a fully self consistent way. The resulting model has only a single phenomenological parameter that may be fit to linear viscoelastic measurements—leaving nonlinear flow predictions without any parameter fitting. A second-order Brownian Dynamics algorithm is used to find stress, optics and conformation predictions in equilibrium and flows.

Tuesday 1:55 Grand Station IV EA7

Developing useful phenomenological rheology models with physically meaningful parameters

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

Practically, it is extremely useful to represent rheological data that spans multiple decades in modulus/viscosity & frequency/shear rate with a model containing a few parameters. The Carreau-Yasuda (CY) viscosity function is perhaps the most popular rheological example of this type, and the Havriliak-Negami (HN) model is the extension of the CY model into the complex plane. Both models achieve their data fitting flexibility by introducing an empirical broadening exponent a to interpolate between the terminal regime and a power-law response $n - 1$ where $0 < n \leq 1$. Recently, J. Janzen and J. Dorgan successfully used the sum of two HN models with fixed $n = 0.03$ to describe the oscillatory shear response of polylactide from the terminal zone to the glassy plateau.

Unfortunately, the HN approach has several difficulties. (1) It is difficult to verify the uniqueness of the answer because the a and n exponents are nonlinearly coupled. To surmount this issue, one can arbitrarily fix n to some small value, usually 0.2 or 0.03. But this procedure compromises the ability to assign physical meaning to both a and n. (2) The low-frequency storage modulus scales as $\log(G') \sim (1 + a)\log(w)$. The correct terminal response is recovered only for the single value $a = 1$.

In this talk, we discuss several alternative approaches to remedy limitations of the CY & HN functions. We employ a generalization of the Cole-Davidson function borrowed from recent work by C. Friedrich. We set exponents to their theoretical values and fit for the scale factors (moduli and relaxation times) separating regimes of response. In analogy with older spectrum models, we compare adding terms to describe each region in series and parallel combinations. The resulting mathematical functions are algebraically more complex than the HN form, but they provide a means of reducing the data in a meaningful manner. The models are evaluated against published data sets for polymer melts with different architectures (linear, branched, etc.).

Tuesday 2:20 Grand Station IV EA8

Nonresonant mechanical hole burning spectroscopy to study dynamic heterogeneity in polymers

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Non-resonant spectral hole burning (NSHB) has proven to be a powerful tool for the investigation of the heterogeneous dynamics in glass forming materials. A mechanical spectral hole burning scheme (MSHB), which is analogous to NSHB was constructed and we investigate the MSHB using two different nonlinear constitutive models: The K-BKZ model and the Bernstein-Shokooh stress-clock model, both of which involve no explicit heterogeneity. In a 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. We verified that the types of material non-linearities represented by the two models cannot reproduce the hole-burning behavior seen in the NSHB experiments. Hence, this provides support for the postulate that NSHB is a means of investigating dynamic heterogeneity. The comparison between the behaviors predicted for the MSHB-type of experiment for the two models shows that for the K-BKZ model a weak non-linearity is imprinted on the response while the Bernstein-Shokooh model, which is also non-linear, shows no evidence that the pulse imprints a signature on the probe response. Preliminary experimental results show interesting and sensitive nonlinear modifications on the linear response. Further experiment and analysis are being carried out. These studies suggest that MSHB offers a powerful tool for the study of the nonlinear viscoelastic behavior of polymers as well as a means of investigating dynamic heterogeneity in polymeric systems.

Tuesday 2:45 Grand Station IV EA9

Dynamical properties of hairy wormlike micelles

Gladys Massiera[1], Laurence Ramos[2], and Christian Ligoure[2]
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Hairy living polymers are obtained by adding amphiphilic copolymer to giant micelles solutions. The presence of copolymer whose hydrophobic part is anchored onto the long lyotropic cylinders induces a drop in static viscosity in the semi-dilute regime, related to a decrease in relaxation times. A shift to higher value of the overlap surfactant concentration is also obtained as copolymer is added. This result demonstrates a strong reduction of the micelles mean length in the presence of copolymer, which is the direct consequence of a decrease of the end cap energy, as demonstrated by dynamic light scattering measurements. Moreover, hairy living polymers are found to be model polymer solutions to address the role of polydispersity in the scaling of the elastic plateau modulus of transient networks. Indeed, allowing only micelles of coil size larger than the mesh size of the entanglement network to contribute to the elasticity, we account for the whole behaviour of the elastic modulus in the semi-dilute regime, and confirm a decrease in the micelles mean length.

Tuesday 3:35 Grand Station IV EA10

Relaxation dynamics of entangled cis-polyisoprene physisorbed at surfaces

Qiang Zhang and Lynden A. Archer
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It is challenging to investigate relaxation dynamics of entangled polymers confined at surfaces. In this study, chain relaxation of entangled cis-polyisoprene (PI) confined in porous glass was studied using broadband dielectric spectroscopy. In our designed model systems, geometric confinement effects are much weaker than surface adsorption effects, allowing relaxation dynamics of surface PI to be determined from the dielectric response. PI in glass pores exhibits two relaxation processes, one fast mode and one slow mode. The fast dynamics are almost independent of polymer molecular weight and appear to be controlled by dynamic adsorption and desorption of chain segments at the surface. The slow dynamics correspond to the global chain relaxation, which is broadened and shifted to lower frequencies compared with the bulk process. The characteristic relaxation time of the slow mode t_s also shows much stronger molecular weight dependence (e.g. $t_s \sim M^{5.7}$ at 30 °C) than the bulk relaxation time t_b ($t_b \sim M^{3.5}$). It is found that surface confinement effects decrease with increasing temperature, increase with increasing polymer molecular weight, and can be largely eliminated by coating the pore walls with a monolayer of oligomers to prevent surface adsorption. The structure of PI at surfaces and molecular mechanisms available for relaxation of adsorbed chains are discussed.

Tuesday 4:00 Grand Station IV EA11

Pressure dependent viscosities and dissipation heating in high shear rate capillary rheometry

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In high shear rate capillary rheometry of polymer melts, both the pressure dependence of shear and elongational viscosities and dissipative heating are no longer negligible. For the determination of the true shear viscosity and its pressure coefficient, it is necessary to develop procedures how to treat and separate the combined effects. As shown by FEM simulations a purely axial temperature profile is sufficient to summarise the effect of dissipation on the observed downstream pressure profile for practical applications. When dealing with the pressure coefficients of viscosity or Bagley correction as determined from throttle experiments, it is important to distinguish between the true pressure effect observed at constant shear stress or apparent coefficients at constant shear rate, respectively. Ignoring the difference may erroneously hint to different pressure coefficients in shear and elongational (entrance) flows. A consistent theoretical description for axial pressure profiles, Bagley plots and throttle experiments has been derived (H. M. Laun, Rheol. Acta (2003), in press) and carefully checked for LDPE and PαMSAN melts.

Tuesday 4:25 Grand Station IV EA12

The effects of supercritical CO_2 and pressure on the rheological properties of a molten polyethylene

Hee Eon Park and John M. Dealy
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Supercritical carbon dioxide (SC-CO_2) is used as a physical blowing agent in the plastic foam manufacture and as a plasticizer to reduce the viscosity in melt processing. Pressure is also an important variable for processing. Thus, the effects of dissolved SC-CO_2 and pressure on the rheological properties must be known to achieve optimum processing conditions. Data reported to date were obtained using capillary or slit rheometers, but the pressure is not uniform in these devices. We used a high-pressure sliding plate rheometer in which the pressure and CO_2 concentration are completely uniform. We measured the effects of dissolved CO_2 and pressure on the viscosity and creep compliance of a high density polyethylene. To separate those two effects, two types of experiments were performed. One was pressurized with no CO_2, and the other was pressurized and saturated with CO_2. The rheometer generates simple shear flow between parallel plates under a hydrostatic pressure that can be controlled independently of the shear rate. The resulting stress is measured using a shear stress transducer. Since the transducer senses the stress in the center of the sample, edge effects are not a problem. It was possible to superpose data for various pressures and CO_2 concentrations to obtain master-curves of the viscosity and creep compliance.

Tuesday 4:50 Grand Station IV EA13

Fast oscillation

Sean W. Race[1], Kaj Hedman[2], and Bing C. Mei[1]
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Historically, oscillation data acquisition consisted of sampling one or more periods and then deriving the real and complex components of the sample response from the measured waves utilizing an FFT. The minimum requirement of a single complete wave cycle has limited the utility of dynamic oscillation to capture very fast changes in material structure such as those that are encountered in UV curing, where the sample may change from a Newtonian liquid to a solid in a few seconds. In recent years, new techniques have been derived to obtain dynamic moduli (or compliance) using 1/4 or 1/2 wave analysis, with the benefit of faster data acquisition, albeit at some compromise in phase angle resolution. A new technique is available for data acquisition that enables the user to acquire oscillation data at intervals as small as 1/100th of a period, with no loss in phase resolution. The principle of data acquisition, analysis, and some examples of its application for characterizing UV curing systems, thixotropic liquid recovery, and thermal transitions is presented.

Symposium MM
Microrheology, Microfluids and MEMS

Organizers: Gerry Fuller and Kalman Migler

Tuesday 1:30 Grand Station V MM20

Dynamics of the interfacial layer between a flowing polymer melt and a solid wall

Mikhail A. Tchesnokov[1], Jaap Molenaar[1], and Johan J. Slot[2]
[1]Electrical Engineering, Mathematics and Computer Science, University of Twente, Enschede, The Netherlands; [2]Science and Technology/Physics of Complex Fluids, University of Twente, Enschede, The Netherlands

In this presentation the dynamics of polymer chains tethered to a solid wall and interacting via entanglements with an adjacent flowing melt of bulk chains is considered within the framework of the rigorous BVPDF approach that was discussed in the previous talk. This problem is believed to be closely related to the problem of spurt flow that is often observed in polymer melt extrusion beyond some critical flow rate. To describe spurt flow macroscopically, it is necessary to know the slip law, which in its simplest form relates the slip velocity to the stresses near the wall. The slip velocity V_s is not the velocity at the wall, but at a microscopic distance h away from it. Once this interfacial layer thickness h is known, V_s can be determined by matching the shear stresses in the interfacial and bulk regions. Therefore, h is the prime quantity of interest and if we know how it evolves in time and how it depends on the various molecular and process variables (molecular weight of bulk and tethered chains, branching content, bulk flow rate etc.), we can in principle determine this slip law. In the presentation we will show how the time evolution equation for h can be derived from the evolution equation for the BVPDF. The resulting equation is highly complicated, but simplifies considerably when the imposed bulk flow rate does not exceed the inverse Rouse time of the tethered chains, the so-called slow flow regime. Results obtained from numerically solving this reduced equation will be presented for the case when the tethered chains are in the so-called "mushroom" regime.

Tuesday 1:55 Grand Station V MM21

Probe surface chemistry and particle size dependence of microrheological measurements in F-actin

Byeong-seok Chae and Eric M. Furst
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Microrheology offers the ability to probe polymer network response over a wide range of timescales (microseconds to seconds) with exquisite sensitivity. However, much has yet to be understood about the effects of local fluid structure and probe particle surface chemistry on microrheological measurements. Recently, it has been shown that the microrheological response in F-actin, a model semiflexible polymer, depends strongly on the surface chemistry of the probe particles [1]. Using diffusing wave spectroscopy to measure the mean-squared displacement of colloidal tracer particles in F-actin, we find that surface chemistries resulting in substantially lower sensitivity to the network correspond with depletion of polymer surrounding the probes. The length scale of the depletion is determined using a shell model to account for the hydrodynamic interactions in a locally heterogeneous material [2]. Unlike recent results reported for entangled DNA solutions, where the local heterogeneity is caused by entropic depletion and scales with the mesh size [3], we find instead that the depleted layer in F-actin scales with size of the tracer particles. We propose that the depletion is due to size exclusion by the probe that results in lower polymer density and reorientation of filaments near the particle surface. By considering the orientation of filaments that are larger than the tracer particles, we show the F-actin contour density surrounding the probes is consistent with the observed dependence on particle size. Furthermore, we find that tracer particle surface chemistries which give good agreement with bulk measurements of the plateau modulus correspond to particles strongly adhering to F-actin filaments. This adhesion results in a breakdown of the generalized Stokes-Einstein relationship dependence on particle size.

[1] McGrath and Kuo, Biophys. J. 79, 3258 (2000).
[2] Levine and Lubensky, Phys. Rev. E 63, 041510 (2001).
[3] Chen et al., Phys. Rev. Lett. 90, 108301 (2003).

Tuesday 2:20 Grand Station V MM22

Membrane and interfacial microrheology

Alex J. Levine[1] and Fred C. MacKintosh[2]
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How can one use fluctuation based measurements to study the rheological properties of two-dimensional structures such as membranes or the surfactant-decorated interface of two immiscible fluids? In this talk we discuss an extension of standard microrheology to such two-dimensional systems; specifically we analyze the fluctuation spectrum of a tracer particle trapped in a viscoelastic membrane/interface that is viscously coupled to a surrounding Newtonian fluid. We demonstrate theoretically how one can use these tracer particle autocorrelations and the correlated fluctuations of two such particles to probe the frequency-dependent shear, compression, bending moduli that interface. In addition we show how to use these results to compute the frequency-dependent mobility of extended objects in the interface.

Tuesday 2:45 Grand Station V MM23

Investigating stress fluctuations and active behavior of living cells

Brenton D. Hoffman[1], Andy W. Lau[2], Tom C. Lubensky[2], and John C. Crocker[1]
[1]Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA; [2]Physics and Astronomy, University of Pennsylvania, Philadelphia, PA

The viscoelastic properties and motion of the cytoskeleton must play a key role in many biologically relevant processes, such as intracellular transport, cell crawling and mechano-chemical transduction. In eukaryotic cells these properties arise from an intricate protein filament network driven by specialized motor proteins and directional polymerization. In this study, multiple particle tracking was used to accurately measure the vector displacements of two cell lines' (J774A.1 mouse macrophages and mouse F9 carcinoma cells) endogenous particles, mainly lipid granules and mitochondria. Then a recently developed tracer correlation technique, two-point microrheology (extended for non-thermal systems), was applied to measure the intrinsic strain fluctuations of the living cell. Spatially, these fluctuations decay as R^{-1}, indicating that the cell may be treated as a coarse-grained continuum on scales of 2 to 8 μm. The temporal behavior can be expressed in the form of ensemble and time averaged mean square displacement (msd) with superdiffusive behavior (msd ~ t^a where $1.3 < a < 1.6$). This combination of properties is indicative of a viscoelastic continuum driven by non-thermal forces with power law rheology. Furthermore, when these fluctuations are combined with recent active cell rheology results the intracellular stress fluctuations may be calculated. The power spectrum of these fluctuations has a nearly $1/\omega^2$ form as expected for a continuum with a slowly varying prestress.

Symposium LC
Liquid Crystalline Polymers and Self-Assembling Fluids

Organizers: Karen Winey and Peter Olmsted

Tuesday 3:35 Grand Station V LC1

Kinetics of shear banding in wormlike micellar solutions probed by simultaneous rheometry and particle image velocimetry

Y. Thomas Hu
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Slip and shear banding in a viscoelastic wormlike micellar system are studied by simultaneous rheological and particle image velocimetry (PIV) methods in a coni-cylinder flow cell. Local flow velocities across the flow cell gap are measured at apparent shear rate from 10^{-3} to 10^{2} s^{-1}. Slip at the flow cell surface occurs at surprisingly low shear rates and increases in magnitude with increasing apparent shear rates. Shear banding in the bulk eventually develops at higher shear rates. The time evolution of the shear banding is investigated by measuring the velocity profile in the gap with a time resolution of 70 ms.

Tuesday 4:00 Grand Station V LC2

Study of the shear banding in wormlike micellar solutions using NMR

M. Rosario López González[1], Panos Photinos[2], and Paul T. Callaghan[1]
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Under appropriate conditions of surfactant concentration, salinity and temperature, surfactants can associate in long flexible wormlike micelles, which show complex behaviour under shear deformation including non-equilibrium phase transitions, flow instabilities and shear banding. Rheological measurements show flow curves where the shear stress presents a double-valued behaviour, that is, the system forms two or more shear bands at two different shear rates with coexistence stress. The volume fractions of these bands are governed by a simple lever rule, $d\gamma = \phi_L\, d\gamma_L + \phi_H\, d\gamma_H$, where ϕ_L and ϕ_H are the volume fractions of the low shear rate and high shear rate. The low and high shear bands have sometimes been associated with isotropic and nematic phases within the fluid.

In this work Nuclear Magnetic Resonance (NMR) spectroscopy and rheology are combined to study wormlike micelle in two systems, namely cetylpyridinium chloride/sodium salicylate in NaCl brine and cetyltrimethylammonium bromide/KBr/H_2O. Both solutions were doped with small amounts (0.1% w) of deuterated n-decane to probe the micellar interiors as a function of shear rate. Shear deformation was induced using a Couette cell in the bore of a 7 T magnet. The ^2H NMR spectra from the d-decane in the micelles were recorded as a function of shear rate up to 40 s^{-1}. These show that the order parameter of the nematic phase remains constant for different shear rates and that the volume fraction of the nematic phase increased with shear rate, as predicted by the lever rule.

Tuesday 4:25 Grand Station V LC3

Tuning rheological properties of cationic surfactant solutions by varying solvent polarity, temperature and counterion concentration

Ying Zhang[1], Judith Schmidt[2], Yeshayahu Talmon[2], and Jacques Zakin[1]
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Some quaternary cationic surfactants, when mixed with a counterion, are known to self-assemble into wormlike micelles in water solvent. Such behavior causes drastic changes in rheological properties of even very dilute solutions, allowing them to be used as drag reducing agents (DRA) in turbulent pipe flow circulating systems, such as district cooling /heating systems (DCS/DHS). Surfactant self-assembly is a physico-chemical phenomenon whose character depends on surfactant concentration, nature of the solvent, temperature and type and concentration of counterions. In this study, rheological properties were investigated for solutions of cationic surfactants, Ethoquad O/12 (oleyl bis(hydroxyethyl) ammonium chloride) and O/13 (oleyl tris(hydroxyethyl) ammonium acetate), with sodium salicylate (NaSal) as the counterion. It was found that the shear viscosity, apparent extensional viscosity and solution viscoelasticity at temperatures from –5 ~ 25ºC can be tuned by modifying solvent polarity (e.g. with additional ethylene glycol (EG) or propylene glycol (PG) in water), changing surfactant concentration and adjusting the counterion to surfactant molar ratio. Cryo-TEM images show the microstructures of wormlike micelles in these systems. The results are related to drag reduction effectiveness and can be used as a guide for improved formulations for low temperature applications DCS using EG/water or PG/water cooling fluids.

Tuesday 4:50 Grand Station V LC4

Transient extensional rheology of wormlike micelle solutions

Jonathan P. Rothstein
Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003

A filament stretching rheometer is used to follow the evolution in the tensile force and the flow induced birefringence of a series of wormlike micelle solutions experiencing a uniaxial elongation flow. The experiments are performed using a series of wormlike micelle solutions of cetyletrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) in deionized water. The linear viscoelastic shear rheology of the wormlike micelle solutions is well described by an upper convected Maxwell model with a single relaxation time. In transient homogeneous uniaxial extension, the wormlike micelle solutions demonstrate significant strain hardening and a failure of the stress-optical, however, no stress-conformation hysteresis is observed. A quantitative fit to the extensional rheology of each of the wormlike micelle solution tested is achieved with a FENE-PM model having as few as two relaxation modes. At a critical stress, independent of strain rate, the wormlike micelle solutions filaments are found to fail through a dramatic rupture near the axial midplane. This filament failure is not the result of elastocapillary thinning as is commonly observed in the filament stretching of weakly strain hardening polymer solutions. The filament failure stems from the local scission of individual wormlike micelle chains. The energy of wormlike micelle chain scission is calculated to be roughly 2 kBT for all the solutions tested, independent of both the imposed extension rate and the concentration of the surfactant and the salt.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Grand Station I/II PL3

Development of the science of rheology since its formal inception

Arthur B. Metzner
Department of Chemical Engineering, University of Delaware, Newark, DE 19716

This presentation will consider the development of our science since the inception of rheology as a distinct area of scientific inquiry in 1929. Emphasis is placed on two general subjects: (a) Continuum analysis and the experimental methods used to evaluate theoretical postulates (b) Progress in the description of non-linear fluids in complex flows, as encountered in polymer processing and in the handling of suspensions Explicitly omitted are considerations of molecular theories, linear viscoelasticity, the rheology of solids and of dry particles, and non-isothermal flows — the first three of these subjects because others are better qualified to describe them and the last because there is as yet very minimal literature on this most ubiquitous of all rheological phenomena encountered in practice.

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Wednesday 9:45 Grand Station I SM28

Effect of the rheology of the suspending fluid on string formation in suspensions

Jan Vermant, Rossella Scirocco, and Jan Mewis
Department of Chemical Engineering, K.U.Leuven, Leuven B-3001, Belgium

An intriguing and long-standing observation is that non-colloidal particles, in dilute suspensions in visco-elastic fluids form necklaces when sheared at sufficiently high shear rates. This has been attributed to normal stress differences, and several authors suggest that a critical Deborah number governs the transition to these particle strings. In the present work, the effect of the visco-elasticity and non-Newtonian behaviour of the suspending fluid on the flow behaviour and the microstructure of the suspension is studied. Different types of suspending media, i.e; Boger fluids, shear-thinning inelastic fluids and various polymer solutions, are used with micrometer sized polystyrene spheres

The microstructure of the suspensions during shear flow is investigated by microscopy and total intensity small angle light scattering. Quantitative results concerning the degree alignment of particles in the different fluids are presented in terms of an alignment factor calculated from the intensity distribution of SALS patterns. The particles are found to align both in the visco-elastic and the viscous shear-thinning fluids when being sheared above a certain shear rate, whereas they do not align either in the Boger fluids or a Newtonian fluid. It is shown that the onset of alignment is not determined by a critical Deborah number as proposed earlier. The SALS results also confirm that the phenomenon is produced in the bulk of the liquid and is not wall-induced.

Wednesday 10:10 Grand Station I SM29

Jamming in concentrated suspensions

Kurt M. Knipmeyer and David J. Pine

Dept. of Chemical Engineering and Materials, University of California, Santa Barbara, CA

We report jamming in dense suspensions of non-colloidal particles. The systems consist of 225-micron particles with 10% polydispersity in a density and refractive-index matched Newtonian solvent. We observe jamming, the intermittent or complete stopping of flow, under an applied stress for particle concentrations exceeding a volume fraction of approximately 50%. Jamming is observed in startup flows and flow reversal. It occurs at low levels of stress for strains less than unity, and depends on the particle concentration.

The occurrence of jamming depends sensitively on the flow history. After having prepared the system in a well-defined state of random particle positions, a constant stress is applied until the system jams. From the jammed state, the flow is reversed; under certain conditions, jamming is again observed. Three distinct behaviors can occur under multiple flow reversals, depending on the applied stress σ: (1) if $\sigma < \sigma_{c1}$, jamming occurs regardless of the number of flow reversals, (2) if $\sigma_{c1} < \sigma < \sigma_{c2}$, jamming occurs at first, but the system eventually flows after a finite number of reversals, (3) if $\sigma > \sigma_{c2}$, the system flows the first time, and jamming is not observed. These critical stresses are dependent on the particle concentration of the system. The critical stresses depend sensitively on the particle concentration and indicate that even in a polydisperse suspension, shear flow can induce ordering of particles to facilitate flow.

Wednesday 10:35 Grand Station I SM30

Direct simulations of particle suspensions of Oldroyd-B fluids in sliding bi-periodic domains: Rheology and microstructural development

Wook Ryol Hwang, Martien A. Hulsen, and Han E.H. Meijer

Materials Technology, Eindhoven University of Technology, Eindhoven 5600MB, The Netherlands

We present a new finite element scheme for direct simulation of inertialess particle suspensions in simple shear flows of Oldroyd-B fluids. The sliding bi-periodic frame of Lees and Edwards [J. Phys. C 5 (1972) 1921] has been combined with the DEVSS/DG finite element scheme, by introducing constraint equations along the domain boundary. The force-free, torque-free rigid body motion of a particle is described by a rigid-ring problem and implemented by Lagrangian multipliers only on the particle boundary, which allows general treatments for boundary-crossing particles. In our formulation, the bulk stress is obtained by simple boundary integrals of Lagrangian multipliers along the domain and particles.

Concentrating on 2-D circular disk particles, we discuss the bulk rheology of suspensions as well as the microstructural development through the numerical examples of single-particle, two-particle and many-particle problems, which can represent an infinite number of such systems under simple shear flow because of the bi-periodicity. We report the steady bulk viscosity and the first normal stress coefficient, from very dilute to highly concentrated systems. The results show shear-thickening behaviour. Unlike Newtonian systems, two particles in an Oldroyd-B fluid result in kissing-tumbling-tumbling phenomena, keeping rotating around each other, when they are closely located.

Wednesday 11:00 Grand Station I SM31

Diffusivities and front propagation in sedimentation

Peter J. Mucha[1] and Michael P. Brenner[2]

[1]Mathematics, Georgia Institute of Technology, Atlanta, GA 30332-0160; [2]Engineering and Applied Sciences, Harvard University, Cambridge, MA

Continuum models for particles sedimenting in a fluid often assume that the diffusion coefficient is a local function of the particulate volume fraction. Under conditions of low Reynolds number and large Peclet number, the effective diffusivity is a direct result of the velocity fluctuations of particles. The recent identification [Tee et al., Phys. Rev. Lett. 89, 054501 (2002)] of particle density stratification as a controlling parameter for the velocity fluctuations then also extends to the effective diffusion coefficient. In particular, the stratification control strongly affects the diffusivity in the vicinity of the falling sediment front between particle-laden fluid below and clarified fluid above. The resulting scaling for stratification-controlled diffusivities in creeping flow sedimentation is presented and compares favorably with measurements from dilute-limit particle simulations. Steadily-falling concentration profiles for dilute sedimentation with these diffusivities are then presented, leading to a surprising reinterpretation of the common wisdom of self-sharpening. Possible extensions of the model to higher volume fractions and to Boycott flows in inclined channels are also discussed.

Wednesday 11:25 Grand Station I SM32

Spin viscosity in suspensions

Shihai Feng[1], Alan Graham[1], James Abbott[1], and Howard Brenner[2]
[1]Chemical Engineering Department, Texas Tech University, Lubbock, TX; [2]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA

In incompressible Newtonian fluids, the shear viscosity is the proportionality constant that relates the flux of linear momentum to gradients in the velocity. Similarly, the spin viscosity is the proportionality constant that relates the flux of angular momentum to gradients in the spin field for simple fluids. In this investigation, the dimensional difference between spin viscosity and shear viscosity predicted by theory is verified. The quantitative values of spin viscosity are determined by calculating the averaged couple stress and kinematics of suspension flow in boundary element simulations. These results are the first reported values for spin viscosity.

Symposium VF
Viscoelastic Flows and Instabilities

Organizers: Jonathan Rothstein and Bamin Khomami

Wednesday 9:45 Grand Station III VF28

Electrification of linear polyethylenes melts under stable and unstable flow

José Pérez-González and Lourdes de Vargas
Laboratorio de Reología, Instituto Politécnico Nacional, México D. F., México D. F. 07051, Mexico

A study of the electrification of linear low-density and high-density polyethylenes under stable and unstable continuous extrusion is presented in this work. The flow experiments were performed at a temperature of 200 °C in a single screw extruder using dies constructed from different materials, meanwhile the electric charge on the extrudates surface was measured with a home-made electrometer. Stable and unstable flow conditions were explored, including slip and no-slip at the die wall. Electric charge on the extrudates was only observed when extrusion under strong slip conditions took place, independently of the polymer. Thus, the electric charge exhibited a maximum as a function of the shear stress under stable flow with slip. In the unstable stick-slip regime, the electric charge oscillated in the same way as pressure did, which suggests an adhesive failure at the die wall in this flow regime.

Wednesday 10:10 Grand Station III VF29

An optimal control formulation for identifying rheological parameters of elastic fluids

Monica F. Naccache[1], Fernando A. Rochinha[2], and Roney L. Thompson[1]
[1]Department of Mechanical Engineering, Catholic University of Rio de Janeiro, Rio de Janeiro, Rio de Janeiro 22453-900, Brazil; [2]Department of Mechanical Engineering, Federal University of Rio de Janeiro, Rio de Janeiro, Rio de Janeiro 21945-970, Brazil

Nowadays, modelling plays a crucial role in controlling and optimizing industrial process by providing means of better understanding involved phenomena and, probably their key feature, of predicting future behavior. The use of such models is mainly based on computational simulations giving rise to two shortcomings concerning the reliability of the results, namely: numerical pitfalls inherent to approximation methods and uncertainties associated to non modelled dynamics and to parameters values. This last drawback can be alleviated by System Identification which consists on the process of improving a mathematical model for a real system by combining physical principles with experimental or field data.

The present work is motivated by the need of improving the capability to predict the sophisticate dynamic mechanical response of non-Newtonian fluids. In this work, numerical data of pressure drop is used as entry data to an optimal control formulation, and rheological parameters for a elongational viscosity model are obtained. The stress field and elongational rates are obtained numerically via a finite volume method, in a 4:1 abrupt axisymmetric contraction flow, using a non-linear constitutive equation (Thompson et al., 1999) to model the non-Newtonian fluid behavior.

The optimal control formulation phrases the identification problem as the search for an optimal set of parameters that minimizes a performance index relating measured pressure drop along the flow with the one predicted by the modelling. The method used for solving the optimization problem is the Conjugate Gradient Method, which is a powerful iterative technique for solving linear and nonlinear inverse problems concerning parameters estimation.

Reference: Thompson, R.L., Souza Mendes, P.R. and Naccache, M.F., J. of Non-Newt. Fluid Mech., 86, p. 375-388, 1999.

Wednesday 10:35 Grand Station III VF30

Tests of time-dependent viscoelastic flow simulations of a shear thinning fluid using axisymmetric flow birefringence

Jason Bryant and Wesley Burghardt
Northwestern University, Evanston, IL

We will present a comprehensive test of time-dependent viscoelastic flow simulations of a shear thinning fluid in an axisymmetric flow geometry. Experiments were conducted on a shear-thinning polystyrene solution in a time-dependent axisymmetric stagnation flow using axisymmetric flow birefringence. Fluid in a closed cylinder is forced periodically past a cylindrical obstruction with a hemispherical cap. Fluid elements near the obstruction thus alternately experience uniaxial and equibiaxial extension on a time scale set by the frequency of the oscillatory motion. This flow is computed with a multi-mode Giesekus model via finite element simulation. The time-dependent axisymmetric stress distribution is numerically integrated to allow direct comparison between computation and birefringence measurements of integrated shear and normal stress distributions as a function of time and position within the flow. The comparison is performed over a grid of experimental conditions in which Deborah number and Weissenberg number are independently varied.

Wednesday 11:00 Grand Station III VF31

Role of inertia and gap temperature on the thermoelastic instability in Taylor-Couette flow

Dennis Thomas, Radhakrishna Sureshkumar, and Bamin Khomami
Washington University, Saint Louis, MO

Recent theoretical [1-2] and experimental [3-4] investigations have shown that thermal effects induced by viscous heating can significantly alter the stability characteristics of viscous and viscoelastic curvilinear flows of thermally sensitive liquids, i.e., liquids with large activation energy associated with viscosity and/or relaxation time (e.g. glycerin, dilute polymer solutions used in investigations of elastic flow instabilities). In the presence of viscous heating the critical shear rate for the onset of viscoelastic instability in Taylor-Couette flow could be an order of magnitude lower compared to its value under isothermal conditions. Under typical experimental conditions the elasticity number, defined as the ratio of the fluid relaxation time to the time scale of viscous diffusion based on the gap width, could reach O(1) or lower values due to thermal effects. Hence, the flow is no longer purely elastic but inertio-elastic. Consequently, the role of inertia has to be included in the stability analysis. Moreover, the temperature difference within the gap plays a key role in determining the critical shear rate. In this work, the role of inertia and the effect of gap temperature on the thermoelastic stability in Taylor-Couette flow are investigated theoretically via linear stability analysis. A comparison of theoretical predictions with experimental data will be presented.

References

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Wednesday 11:25 Grand Station III VF32

Purely elastic instabilities in non-viscometric viscoelastic flows

Balraj Sadanandan and Radhakrishna Sureshkumar
Washington University, Saint Louis, MO

Accurate prediction of the stability dynamics of viscoelastic flows is germane to the design and control of polymer processing operations. Many studies to date have dealt with linear and non-linear stability characteristics of viscometric flows. However, relatively fewer studies have analyzed the linear and non-linear stability characteristics of mixed-kinematics flows, i.e., flows with both shear and extensional characteristics. We present the results of a stability analysis of the flow of an Oldroyd-B fluid in a Periodically Constricted Channel. Local linear stability analyses have been already performed for this flow (Sureshkumar, JNNFM, 97: 125 (2001); Sadanandan and Sureshkumar, JNNFM, 108: 143 (2002)). However global (non local) effects could be significant for O(1) values of the Weissenberg number, especially if long and moderately large wave perturbations are included. This motivates the need for global stability analysis performed in this study. We use a Chebyshev-Fourier collocation method on a staggered grid to simulate the base flow. We then employ sub-matrix based transformations and direct time-integration to solve the eigenvalue problem resulting from the linear stability analysis. The physically relevant eigenvalues are isolated from the spurious ones by systematic mesh refinement. Our studies revealed a purely elastic instability even in the absence of base flow separation. A mechanical energy budget analysis indicated that the destabilization arises due to the coupling between base flow shear velocity gradients and the perturbation stress. We next study the non-linear stability against finite amplitude disturbances. Since fully implicit time integration for multi-dimensional viscoelastic flows is an extremely computationally intensive task, we will employ a semi-implicit operator splitting scheme with an influence matrix correction. The results will be used to perform a bifurcation analysis.

Symposium EA
Entangled Polymers and Analytical Rheology

Organizers: Monty Shaw and James P. Oberhauser

Wednesday 9:45 Grand Station IV EA14

Solution rheology of entangled polymer mixtures

Shanfeng Wang[1], Shi-Qing Wang[1], Adel Halasa[2], W.-L. Hsu[2], J.P. Zhou[2], and R.P. Quirk[1]
[1]University of Akron, Akron, OH; [2]Goodyear, Akron, OH

One of the first steps toward understanding melt rheology of polymers with broad molecular weight distribution (MWD) is to establish rheological characteristics of the same polymers with a bimodal MWD, i.e., binary mixtures at all compositions. Recently we have made some progress [1] toward this goal for such binary mixtures where the high MW component's weight fractions are high enough to be self-entangled all the way up to pure long chains. Systematic experimental data were used to extend the previous theoretical description of chain dynamics in such entangled mixtures. On the opposite dilute limit of the long chains, theoretical treatment, based on scaling arguments involving such important concepts such chain reptation and constraint release through tube reorganization, can be readily developed to provide predictions on such properties as the intrinsic viscosity as a function of both long and short chain lengths NL and NS. This talk focuses on the comparison the theoretical predictions and rheological measurements of mixtures made of the entangling long chains dissolved in matrices of short chains of length NS with either NS > Ne or NS < Ne, where Ne is the critical chain length for entanglement. This investigation allows us to establish the tracer chain dynamics in the various regimes as described in the companion paper [2].

[1]Shanfeng Wang et al. “Relaxation Dynamics in Mixtures of Long and Short Chains: Tube Dilation and Impeded Curvilinear Diffusion”, Macromolecules, in press (2003).
[2]Shanfeng Wang et al., “Diffusion and Rheology of Entangled Binary Mixtures”, presenting in the same Entangled Polymers and Analytical Rheology Session.

Wednesday 10:10 Grand Station IV EA15

Rheological characterization of polymer melts with narrow molecular weight distribution

David Venerus[1] and Thomas Schweizer[2]

[1]Department of Chemical Engineering, IIT, Chicago, IL 60616; [2]Institute for Polymers, ETH, Zuerich, Switzerland

The flow behavior of entangled linear polymers with narrow molecular weight distribution has been the subject of numerous experimental and theoretical studies. Due to the experimental difficulties associated with the rheometry of polymer melts, most experimental studies have focused on polymer solutions. In addition, the majority of data on well-characterized polymer liquids are limited to the shear viscosity and first normal stress difference. Measurements of the second normal stress difference in shear and elongational viscosity are even more scarce. The absence of comprehensive data sets on well-characterized polymer liquids is a serious problem for theoreticians seeking to develop predictive rheological models. In this study, we have carried out comprehensive rheological tests on linear polymer melts with narrow molecular weight distribution. Data have been obtained on poly-styrene and poly-isobutylene melts with approximately 15 entanglements per chain. In transient shear flows, the full stress tensor has been measured mechanically for both melts. In addition, both the stress and birefringence have been measured in transient uniaxial elongation flows of the polystyrene melt. Comparisons of these data with tube model predictions will also be presented.

Wednesday 10:35 Grand Station IV EA16

Effects of polydispersity on the rheological properties of entangled polystyrene solution

Xiangnan Ye and Tam Sridhar

Department of Chemical Engineering, Monash University, Clayton, VIC 3180, Australia

In order to investigate the effects of polydispersity on rheological properties of entangled polystyrene solution, a polydisperse blend with average molecular weight of 2.89×10^6 is made by mixing 19 components of nearly monodisperse polystyrene. The weight fraction of each component was so calculated to obtain a polydispersity of 3.5 for the blend, by assuming all polymers have Log-Normal distributions. The polydisperse system has much broader relaxation spectrum and its zero-shear-rate viscosity is slightly less than that of monodisperse solution with same molecular weight and concentration. Within a large strain-rate region, the polydisperse blend shows shear thinning, same as those for monodisperse systems. On the other hand, the polydisperse blend has much higher extensional viscosity and stronger strain hardening over a wide range of strain rates, possibly due to the presentence of high molecular weight. In addition, following the success of the "toy" Mead-Larson-Doi (TM) model in predicting the behaviour of bidisperse solutions, it is expected that the TM model will work for the general polydisperse systems. The TM model is also examined for the predictions of both linear viscoelastic and extensional properties of this polydisperse system by using parameters obtained from the corresponding monodisperse polymers.

Wednesday 11:00 Grand Station IV EA17

Effect of molecular architecture on the rheology of polymer blends: Birefringence and rheo-FTIR

Semen B. Kharchenko[1] and Rangaramanujam M. Kannan[2]

[1]Polymers Division, NIST, Gaithersburg, MD 20899-8544; [2]Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Controlling the branching (architecture) of polymers can result in novel, technologically beneficial properties. Highly branched polymeric materials exhibit significantly different rheological behavior compared to linear polymers, which is a subject of experimental and theoretical interest. We are studying the mechanical and rheo-optical behavior of series of custom-synthesized symmetric stars, and controlled-branch length hyperbranched polystyrenes (HBPS), where the arms are relatively unentangled. Our results suggest that the branch density plays a vital role on the orientation behavior, as suggested by the non-terminal behavior in rheology, and the failure of the stress-optical rule even for the homopolymer melts, when the branch density is high. The unusually large birefringence from the homopolymers appears to be due to the form birefringence from the core-shell morphology exhibited by the highly branched homopolymers.

Results on HBPS/linear PS blends, and HBPS/PVME blends suggests that the high branch density may also affect the blending behavior to a significant extent. In contrast to a linear PS/PVME blend that shows a breakdown in time-temperature superposition (TTS) even in the miscible state, blends of HBPS/PVME show no breakdown in TTS even when HBPS is the majority component. The glass transition behavior of the blends are not appreciably different. This suggests that high branch density may be preventing PVME from entering the core of the HBPS. Therefore, the segments of PS near the periphery of HBPS may be miscible, but the segments near the core would be immiscible, resulting in a 'molecularly dispersed' blend, rather than a segmentally miscible blend, as in the case of linear PS/PVME blends. The difference in the PS and PVME contributions to the blend dynamics, arising as a result of differences in the architecture are being probed using quantitative flow birefringence and rheo-FTIR measurements.

Wednesday 11:25 Grand Station IV EA18

Diffusion and rheology of entangled binary mixtures

Shanfeng Wang[1], Ernst von Meerwall[1], Shi-Qing Wang[1], Adel Halasa[2], W.-L. Hsu[2], J.P. Zhou[2], and R.P. Quirk[1]

[1]University of Akron, Akron, OH; [2]Goodyear, Akron, OH

This presentation discusses the diffusion and rheological behavior of binary mixtures (of long and short chains) based on 1,4-polybutadiene over the full composition range as a function of both long and short chain lengths using pulse-gradient NMR and oscillatory shear measurements. The first set of rheological and diffusion measurements reveals that the terminal relaxation rate and self-diffusion coefficient D_s of the long chains decrease systematically with increasing short chain length NS and with the weight fraction of the long chain in the mixtures. These observations can be understood in terms of chain reptation in a dilated tube with a coarse-grained curvilinear diffusivity, a notion proposed recently for chain dynamics in entangled binary mixtures. The second set of data indicates that the short chain's diffusion coefficient D decreases with increasing, leading to an insightful comparison between the self-diffusion coefficient D_s and tracer diffusion coefficient D_{tr}: D_{tr} recovers the asymptotic molecular weight scaling of $M^{-2.0}$ whereas D_s scales non-ideally as $M^{-2.4}$ due to the considerable constraint release effect in the explored range of molecular weight. These experimental observations along with additional theoretical analyses have allowed a clear identification of different regimes in a dynamic "phase" diagram where the two axes are the probe chain's molecular weight M and matrix molecular weight P respectively. The different regimes for the probe chain dynamics are (1) Zimm dynamics, (2) Rouse dynamics, (3) non-ideal reptation due to the acceleration by constrain release, (4) Rouse dynamics of tube re-organization, (5) Stokes-Einstein regime and (6) pure chain reptation dynamics. A companion paper presents the rheological identification of some of these regimes in detail [1].

[1] Shanfeng Wang et al., "Solution Rheology of Entangled Polymers", presenting in the same Entangled Polymers and Analytical Rheology Session.

Symposium LC
Liquid Crystalline Polymers and Self-Assembling Fluids

Organizers: Karen Winey and Peter Olmsted

Wednesday 9:45 Grand Station V LC5

Sharp-interface description of isotropic-nematic phase transitions

Eliot Fried

Theoretical and Applied Mechanics, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Sharp-interface theories have been developed to describe material interfaces between nematic and isotropic fluids. These theories account for flow, director elasticity of the nematic fluid, and anchoring energy at the interface. Here, we discuss the extension of such theories to account for phase transitions. Such transitions involve the growth of one phase, nematic or isotropic, at the expense of the other, as described by the motion of the interface. A key ingredient of the theory is a supplemental interface condition of Gibbs-Thomson type. We apply the theory to study the behavior of an isotropic spherical drop surrounded by a uniaxially-aligned nematic phase. The free-energy density of the nematic phase measured relative to that of the isotropic phase determines whether or not the drop decays, grows, or stabilizes. Under certain conditions, we find that there exist two stable radii for the drop.

Wednesday 10:10 Grand Station V LC6

Regular and chaotic rheological behavior of tumbling nematic liquid crystals

Siegfried Hess
Institut f. Theoret. Physik, TU Berlin, Berlin D-10623, Germany

The theoretical analysis of the orientational dynamics of a tumbling nematic liquid crystal subjected to a steady shear flow reveals a complex time dependence of the molecular alignment including chaotic behavior. This was inferred from a solution of a 65 dimensional dynamical system [1] based on a generalized Fokker-Planck equation, and from a closed nonlinear relaxation equation for the alignment tensor, which is equivalent to a 5 dimensional dynamical system [2]. This equation is also derived from the generalized Fokker-Planck equation [3]. Due to the coupling between the friction pressure tensor and the alignment tensor [4], the rheological properties, viz. the shear stress and the normal stress differences of such a nematic also show a chaotic behavior in certain ranges of the relevant control variables, viz. the shear rate and tumbling parameter. Examples for the regular and the chaotic rheological behavior which follow from [2] are presented and discussed. Long time averages are evaluated both for prescribed values of the shear rate and of the shear stress. For selected state points the time dependence of the alignment and of the components of the stress tensor are analyzed for step-like and ramp-like shear rates as well as for reversal of the imposed shear rate.

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Wednesday 10:35 Grand Station V LC7

Structure phenomena of nematic polymers flowing between parallel plates

M. Gregory Forest[1], Qi Wang[2], Hong Zhou[3], and Ruhai Zhou[1]
[1]Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250; [2]Mathematics, Florida State University, Tallahassee, FL; [3]University of California at Santa Cruz, Santa Cruz, CA

We idealize to study one-dimensional gap structures in the flow of nematic polymers in plane Couette cells. A mesoscopic Doi-Marrucci-Greco model is explored, allowing for flow coupling to short-range excluded-volume and long-range distortional elasticity potentials. We begin with a slow plate (small Deborah number) limit, where exact flow-nematic structures reveal permeation modes that span the entire gap together with boundary layer modes localized at the plates. Explicit, multiple scaling properties are identified. We identify Ericksen and Deborah number regimes where new resonant structures emerge as the asymptotics breaks down. Finally, we report numerical studies for general regimes and focus on the correlation between structure generation and bulk monodomain attractors that are presumably resonated in the interior at onset of plate motion.

Wednesday 11:00 Grand Station V LC8

Multiscale modeling of liquid crystal polymers through kinetic and phenomenological approaches

Qi Wang[1], M Carme Calderer[2], and M. Gregory Forest[3]
[1]Mathematics, Florida State University, Tallahassee, FL; [2]Mathematics, University of Minnesota, Minneapolis, MN; [3]Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250

We will present a kinetic framework for the derivation of hydrodynamic theories accounting for multiscales in flows of liquid crystal polymers and multiple interactions. The theory extends the existing ones, represented by the Doi theory for homogeneous liquid crystal polymers, to account for possibly molecular chirality, multiple intermolecular interactions, and size distributions of the liquid crystal polymers. The theory can be applied to extended nematics,

cholesterics and of course nematics with a size fluctuation. We then present model predictions in simple flows such as shear and extensional flows.

Wednesday 11:25 Grand Station V LC9

A diffuse-interface method for simulating the deformation and retraction of liquid crystalline drops

Pengtao Yue[1], James J. Feng[1], Chun Liu[2], Jie Shen[3], and Chixing Zhou[4]
[1]Levich Institute, City College of New York, New York, NY 10031; [2]Department of Mathematics, Pennsylvania State University, University Park, PA 16802; [3]Department of Mathematics, Purdue University, West Lafayette, IN 47907; [4]Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

In this talk, we present an energy-based method for treating interfacial problems involving rheologically complex fluids. Introducing a phase-field variable to describe the interface, a set of governing equations are derived for all phases which hold uniformly across interfaces. This greatly simplifies the computational task since the interface no longer needs to be tracked. The surface tension comes out naturally from the minimization of the mixing energy in the phase-field formulation. The energy-based formalism is particularly convenient for incorporating complex rheology since the latter is often derivable from a free-energy as well. Using a spectral implementation, we will describe numerical results on the deformation and retraction of nematic drops in a polymer matrix. The drops will be modeled by a regularized Leslie-Ericksen theory while the matrix by a Newtonian or Oldroyd-B constitutive equation. We will present numerical results on the complex coupling among the molecular orientation in the drop, its deformation and external flow. These will then be compared with experiments that use retracting drops to measure the dynamic interfacial tension between a liquid-crystalline and a flexible polymer.

Wednesday Afternoon

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Wednesday 1:30 Grand Station I SM33

Nonlocal electrostatics and structural coarsening in electrorheological fluids

Daniel Klingenberg[1] and Jeffrey F. Morris[2]

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The transient rheological response of electro- and magnetorheological fluids in simple shear flow is intimately associated with slow changes in structure that occur after an external electric or magnetic field has been applied. Following an initial, rapid formation of fibrous aggregates oriented in the direction of the applied field, the suspension structure slowly rearranges to form stripes of high particle concentration oriented in the direction of flow. The apparent rheological properties of the suspension evolve as these stripe structures slowly coarsen. While the initial fibrous structure can form within 1-100 ms, the stripes, as well as the rheological properties, can continue to evolve over many tens of minutes.

We have previously developed a continuum model to describe structure evolution in ER fluids. By including local electrostatic and hydrodynamic contributions to the stress, a two-fluid continuum model can successfully capture the formation of columns in quiescent suspensions, and the formation of stripes in sheared suspensions. Predictions of the initial stages of stripe formation as well as the steady-state structure agree qualitatively with experimental observations.

Capturing the evolution toward steady-state requires the incorporation of nonlocal electrostatics. In this presentation, we will present a self-consistent, mean-field model for the nonlocal electrostatics in sheared ER suspensions. We will show how nonlocal effects influence the coarsening of stripe structures as well as the transient rheological response. Results will be compared with microscopic models of ER suspensions (e.g., particle-level simulations) as well as experimental observations. Extension of this analysis to MR suspensions in which particle magnetization is nonlinear will also be discussed.

Wednesday 1:55 Grand Station I SM34

Steady and transient shear flow of magnetic dispersions: Structure and rheology

Meihua Piao, Alan M. Lane, and John M. Wiest

Chemical Engineering, University of Alabama, Tuscaloosa, AL 35487

Concentrated dispersions of nanoscale, acicular, ferromagnetic particles are used extensively in the manufacture of data storage materials. These dispersions exhibit striking non-Newtonian and viscoelastic behavior; they are very shear thinning, they show dramatic overshoots on the inception of shear flow, and they have a substantial storage modulus in small amplitude oscillatory shear flow. Here we present a compilation of rheological and neutron scattering results for the dispersions, and we interpret these results in terms of several structural models. Mean field models work well for steady flows, but a more detailed description of many-particle effects seems to be required to describe transient behavior.

Wednesday 2:20 Grand Station I SM35

Magnetorheological suspensions: Rheology and applications in controllable energy absorption

Suraj S. Deshmukh and Gareth H. McKinley

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Magnetorheological (MR) fluids are an important class of 'field-responsive' fluids that have been investigated for application as energy-absorbing materials. The linear-viscoelastic and viscometric properties of these fluids undergo large reversible changes in the presence of applied magnetic fields and field gradients. A fixture for applying nearly uniform magnetic fields up to 0.4 T was custom-built for TA Instruments AR1000/2000 rheometers. Magnetorheological fluids based on different carrier fluids, with or without viscoplastic additives, have been prepared and the dependence of the yield-stress on the magnetic field strength has been compared to commercially available MR fluids. Carbonyl iron particles of different sizes are used to quantify particle size effects on the rheology. Slip in these fluids has been studied for different gap separations and roughened plates are utilized to counter the observed slip. Analysis of creep behavior of MR fluids below the yield stress is particularly useful in providing information on the response time and rheological properties of such field-responsive fluids. A controllable energy-absorbing material consisting of an elastomeric foam impregnated with a field-responsive fluid has been designed and mechanical properties of the resulting composite (i.e. the compressive stress-strain response) have been determined. The viscoplastic flow of the micron-sized MR particles inside the pores of the reticulated foam alters the mechanical properties of this fluid-solid composite. The energy absorbing capacity shows a dramatic increase (by up to 30 times that of the 'dry' foam) due to viscous dissipation in the pores and stiffening of the cellular foam edges. This can be user-controlled by changing the magnetic field to vary the yield-stress of the MR fluid inside the foam pores. The composite materials thus have tremendous potential as adaptive energy absorbers.

Wednesday 2:45 Grand Station I SM36

Induced particle aggregation in suspensions: Effect on rheological properties

Frank E. Filisko[1], Rachel Lynch[1], and Yonggang Meng[2]

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The unique properties of suspensions vs. homogenous fluids are due primarily to the interaction of the particles, i.e. Bingham fluids, thixotropic fluids, etc. While for such fluids the effects are spontaneous and related to the characteristics of the particle and fluid phase, in many suspensions the interactions between the particles (and fluid) can be induced by the application of external electromagnetic fields. While probably the best known of these are the viscous properties of certain suspensions under shear, i.e. electro- and magneto-rheological fluids, others of interest include active control of the morphology of the particle aggregates as well as properties of such suspensions under compression. In the latter case such inductively associated particles structures in suspensions can support stresses in the 10 MPa range which collapse when the fields are removed. In this paper we will discuss current results regarding both induced patterning of particle structures and the compressive properties mentioned above. Other consequences of these phenomena will also be discussed.

Wednesday 3:35 Grand Station I SM37

Rheology of multi-walled carbon nanotube suspensions

Erik K. Hobbie[1], Sheng Lin-Gibson[1], Howard Wang[2], Jai A. Pathak[1], and Eric Grulke[3]

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We present experimental results on the steady shear and oscillatory shear rheology of Multi-Walled Carbon Nanotube suspensions in polyisobutylene (PIB) of low molecular weight (Newtonian) and also in a Boger fluid of PIB. We have found that under conditions of weak steady shear the suspensions in Newtonian PIB show an elastic instability due to flow-induced clustering in the vorticity direction. We suggest that this instability is characteristic of a broad range of complex fluids, and is a local manifestation of the rod-climbing instability. Oscillatory shear experiments show that the addition of Carbon nanotubes to PIB qualitatively affects the response of the fluid. Under conditions of ambient temperature and with small strain amplitudes that correspond to the linear viscoelastic regime, we find a fascinating transition in the response of the fluid from liquid like at high frequencies (the loss modulus G''

exceeds the storage modulus G' by an order of magnitude) to weakly solid-like when at lower frequencies G' and G'' cross over (with G' weakly exceeding G'') and suggest the formation of a weak physical network in the fluid. We are investigating the influence of important variables such as temperature and composition on the rheology of these suspensions, and these results will be discussed.

Wednesday 4:00 Grand Station I SM38

Orientation effects on the capillary instabilities for thin liquid crystalline fibers embedded in a flexible polymer matrix

Jian Wu and Patrick T. Mather
University of Connecticut, Storrs, CT 06269

In this study, we investigated the orientation effects on the capillary stabilities of liquid crystalline polymer (LCP) fiber embedded in one miscible flexible polymer matrix [poly(dimethyl siloxane) (PDMS)] using breaking thread method (BTM). Capillary instabilities, driven by interfacial stresses, are characterized by apparent interfacial tension for oriented and disoriented LCP fibers (PSHQ6,12) in PDMS, which are determined from the transient breakup of a long thread with time. Our experimental results show that the apparent interfacial tension for oriented (as-spun) LCP fibers is several-fold larger than that of disoriented (previously "cleared"), but nematic, LCP fibers at the same temperature. On crossing the transition from a nematic to isotropic phase of the LCP, the apparent interfacial tension features a stepwise increase similar to the steady shear viscosity of the LCP. To better understand our observations, we have employed real-time retardance and orientation imaging during the break-up of the LCP fibers in PDMS. At the early stages, annealing oriented nematic LCP fibers results in banded structures. Later, during the transient breakup stage, such banded structures remain in the large diameter regions but disappear in the small diameter regions, where extensional flow is significant. In contrast, disoriented nematic fibers do not display such phenomena. With such data, we are attempting to determine the role of nematic orientation in the nematic LCP fiber on the capillary instabilities.

Wednesday 4:25 Grand Station I SM39

Experiments and modeling for a time dependent thixotropic suspension

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Time-dependent thixotropic hysteretic rheological behavior is seen in a number of systems from buttermilk and yogurt to colloidal suspensions of particles. At Sandia, we work with a particle-filled epoxy encapsulant that exhibits similar time dependent behavior despite the fact that the particle are quite large (10 micron average diameter) and noncolloidal. This time-dependent behavior is most often linked to structure formation in the suspension or emulsion. For our encapsulant, we theorize that particle networks are forming due to a reaction of the curative with the surfaces of the alumina particles, which leads to agglomeration and structure formation. Thus our system exhibits two concurrent networks: the polymerization of the epoxy and the agglomeration of the particles. To decouple the two networks, we have developed a model system that contains only the particles and the curing agent, without the epoxy monomer. We have carried out step shear experiments with the model system to better understand its transient behavior. A finite element model has also been developed based on a generalized Newtonian formalism that relates the viscosity to the local structure via an evolution equation. Computational results are compared with validation data from step-shear experiments in a Couette viscometer. Agreement between the experiments and simulations has been relatively good given the simplicity of the model.

Wednesday 4:50 Grand Station I SM40

Collision efficiency of orthokinetic agglomeration of particulate suspensions subjected to polymer bridging flocculation

Sushant Agarwal[1], Rakesh K. Gupta[1], and Deepak Doraiswamy[2]
[1]Chemical Engineering, West Virginia University, Morgantown, WV 26506; [2]National Starch and Chemical Company, Bridgewater, NJ

This study examines the problem of shear-induced or orthokinetic agglomeration of particles such as fillers and pigments in polymer solutions where polymer molecules adsorb on the surface of particles and form a bridge. The

agglomeration of particles leads to the demixing of initially well-dispersed suspension. The rate of agglomeration is usually obtained by multiplying the rate of collision of particles by the collision efficiency. In case of polymer bridging, the collision efficiency is usually determined by probabilistic models based on fractional surface coverage of particles by the adsorbing polymer. These models neglect the influence of hydrodynamic forces which must be accounted for when studying shear-induced agglomeration.

In this work, a new model to determine collision efficiency is developed in terms of dimensionless parameters which represent relative magnitudes of van der Waals' attractive force, electric double-layer repulsion, steric interaction and hydrodynamic force. This model is suitable for non-colloidal size particles whose surface is completely covered with the adsorbed polymer.

To validate this model, experimental collision efficiencies at various agglomeration conditions were determined by shearing a model suspension in a cone-and-plate device. The model suspension consisted of 4.9 micron size spherical hollow glass beads dispersed in an aqueous glycerin solution; polyethylene oxide was used as the flocculant. Using experimental collision efficiencies and non-linear regression analysis, the parameters in the collision efficiency model were determined.

It was found that increasing the shear rate decreases the collision efficiency and it can be expressed as a power law. Moreover, at high flocculant concentration, the collision efficiency is less dependent on the shear rate. Increasing the molecular weight and concentration of flocculant also gives higher collision efficiency.

Wednesday 5:15 Grand Station I SM41

Nanoparticles induced non-Einstein like behavior of polymer melts

Anish Tuteja[1], Michael E. Mackay[1], and Craig J. Hawker[2]
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Particulate fillers have long been blended with polymer melts to improve their properties. However, in general these fillers have not been small enough to influence the dynamics at a molecular scale. The linear polymers chosen for this research have a radius of gyration (R_g) between 5-20 nm, while the 'fillers' (special polystyrene nanoparticles) have an R_g of order 5 nm, which is in the prescribed range to affect the polymer chain dynamics.

In general, the addition of fillers to polymer melts increases the viscosity of the melt phase. Einstein first predicted this phenomenon nearly a century ago. Since then various experiments, theoretical modeling and simulations have confirmed this prediction. However, in our case, the addition of these polymer nanoparticles to linear polymers decreases the viscosity of the polymer melts—a result at odds with Einstein's prediction! The effect of changing both the concentration of the nanoparticles and the type of polymer to which these are added is discussed in this presentation. Dynamic light scattering and intrinsic viscosity experiments are used to confirm the size range of the nanoparticles, while rheometry, DSC and DMTA are used to test the physical and transport properties of the blends.

Symposium BR
Biorheology

Organizers: Robert Armstrong and Patrick Doyle

Wednesday 1:30 Grand Station III BR1

Mechanical properties of living cells measured by magnetic twisting cytometry

Gladys Massiera and John C. Crocker
Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA

We use a magnetic bead to probe the rheology of the cytoskeleton of a living cell. The RGD-coated bead is first specifically linked to the cytoskeleton network via integrins, and then magnetized vertically. Applying an oscillating horizontal magnetic field, we torque the bead and exert a stress onto the cytoskeleton. The deformation generated is then computed from the bead's center of mass displacement. Measurements performed on long time (30 min) show fluctuations with a characteristic time on the order of 100 sec. These fluctuations may arise from either our coupling

(e.g. the exchange between integrins in the cell membrane and integrins linked to the bead) or changes in intracellular rheology. Aside from the insights we may gain into the role of integrins in cellular adhesion, we can correct for these fluctuations to improve rheological measurements. This allows high-precision measurements of the frequency dependence of the cytoskeleton's dynamic shear modulus. This should enable studies, such as cell to cell variation, which would likely be difficult or impossible using ensemble averaged measurements.

Wednesday 1:55 Grand Station III BR2

Microrheology and adhesion in cellular systems

Anne A. Leyrat[1], Elisabetta Canetta[1], Roxana Chotard-Ghodsnia[1], Claude Verdier[1], and Alain Duperray[2]
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Cellular systems (i.e. individual cells or tissues) are investigated using a modified JKR [1] technique in order to have access to their elastic and adhesive properties. The experiments are based on the AFM technology, except that a functionalized bead is glued onto the AFM cantilever [2] so that the contact is a sphere-plane one. The experiment is set on an inverted microscope equipped with Phase contrast, RICM and Fluorescence. Results concerning the interaction between cancer cells and endothelial cells will be presented. The levels of adherence are modified by genetically forcing the cells to express different kinds of adhesive protein complexes at their surface. Elastic moduli as well as surface energy values are measured and are found to be in good agreement with the literature.

Another way to measure adhesion is by pulling the bead away from the surface of the cell. In such a case, the time-dependent mechanical response of the cell is measured together with the detachment of cell clusters at the interface. This leads to a representation of the force vs. loading rate which can be interpreted using the Evans –Ritchie's model [3]. The same cellular systems are considered again and application to cancer metastasis will be discussed.

[1] Johnson KL, Kendall K, Roberts AD, Surface energy and the contact of elastic solids, Proc. R. Soc. Lond., A324, 301-313 (1971)
[2] E. Canetta, A. Leyrat, C. Verdier, A physical model for predicting the adhesion between a functionalised microsphere and a living cell, in presse, Math. Comp. Modelling (2003)
[3] Evans E, Ritchie K, Dynamic strength of molecular adhesion bonds, Biophys. J., 72, 1541-1555 (1997)

Wednesday 2:20 Grand Station III BR3

Affine versus nonaffine deformations of semiflexible polymer networks

David A. Head[1], Alex J. Levine[2], and Fred C. MacKintosh[1]
[1]Physics and Astronomy, Vrije Universiteit, Amsterdam, Amsterdam 1081 HV, The Netherlands;
[2]Department of Physics, University of Massachusetts, Amherst, IL 01003

Networks of filamentous proteins play a crucial role in cell mechanics. These cytoskeletal networks, together with various crosslinking and other associated proteins largely determine the (visco)elastic response of cells. The response of these networks is shown to be highly non-linear, and the shear moduli can vary by orders of magnitude with small changes in density and local network connectivity. We discuss a model cytoskeletal network of cross-linked, stiff filaments in order to explore the connection between the network microstructure and the macroscopic response of the network. We find a crossover from affine to non-affine response of these semi-flexible polymer networks. Interestingly, this crossover is completely separate from rigidity percolation in such systems, which we also discuss. We present scaling arguments that capture the essence of this intriguing breakdown of continuum elasticity on mesoscopic length scales in the system.

Wednesday 2:45 Grand Station III BR4

Micromechanics of self-assembling peptides

Thierry Savin and Patrick Doyle
Chemical Engineering, MIT, Cambridge, MA

We have studied the micromechanics of KFE8 peptide gels using multiple particle tracking (MPT), AFM and quick-freeze TEM. Nearly a decade ago Zhang and coworkers [1] discovered this new class of biomaterials formed from the self-assembly of small self-complimentary oligopeptides. MPT allows us to follow the evolution of the microrheology of the system during gelation. Individual studies of the probe colloids at different gelation times show the evolution of spatial heterogeneity in the gel. Time averaging is performed on these individual tracks to analyze local structural and micromechanical properties. These results are compared to detailed images of the gel structure obtained using quick-freeze TEM and AFM.

[1] S. Zhang, T. Holmes, C. Lockshin and A. Rich, PNAS, 90:3334-3338, 1993.

Wednesday 3:35 Grand Station III BR5

Parameter-free predictions of the behavior of dilute polymer solutions in extensional flows: Comparison with experiment

Ranganathan Prabhakar and Jagadeeshan Ravi Prakash
Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

Recent experiments show that the rheological response of dilute polystyrene solutions to the sudden imposition of a constant uniaxial elongation rate, can be collapsed onto master curves when interpreted in terms of suitable variables [Gupta et al., Phys. Fluids, 12 (6), 2000]. In particular, it is observed that the ratio Tr/cM (where Tr is the Trouton ratio, c is the mass concentration and M is the polymer's molecular weight), is a function solely of the Hencky strain, and the Weissenberg number, for a wide range of molecular weights. There are no theoretical predictions to date of this experimentally observed universal behavior. Since universal behavior is a consequence of the self-similar character of long polymer chains, this study uses Brownian dynamics simulations, to predict the rheological behavior of a bead-spring chain model for the polymer, in the long chain limit. Earlier attempts at using simulations of bead-spring chains to predict this behavior have captured the qualitative features of the stress growth but are quantitatively inaccurate. These simulations did not take into account fluctuating hydrodynamic interactions between the beads, which are known to be crucial for the accurate prediction of viscoelastic phenomena. We investigate the role played by fluctuating hydrodynamic interactions in determining extensional flow behavior, and observe that the predictions of transient and steady state properties become independent of the hydrodynamic interaction parameter, h^*, in the limit of long chains. We find that these parameter-free predictions are in quantitative agreement with experimental data for dilute solutions of $M = 1.95$ million polystyrene, for a wide range of Weissenberg numbers. This strongly suggests that fluctuating hydrodynamic interactions may be the key to predicting the observed universal behavior in extensional flows.

Wednesday 4:00 Grand Station III BR6

Conformational and stress relaxation of initially straight flexible polymers

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

The present talk focuses on the relaxation of a single flexible polymer chain from an initial straight configuration in a viscous solvent. Physically this problem may correspond to the case of a polymer chain fully stretched by an (infinitely) strong flow and then relaxed by switching the flow off. As it is well known, large stresses are developed even in dilute polymer solutions involving fully stretched polymer chains. This problem is also motivated by recent experiments with single DNA molecules relaxing after being fully extended by applied forces.

To study this problem, Brownian Dynamics simulations based on a discretized version of the wormlike model are employed over a broad range of time scales and polymer lengths. The relaxation of the full stress tensor is presented which at long times approaches equilibrium with a slower relaxation rate than that predicted by the Rouse theory. An explanation for this discrepancy is provided. For the first time the configuration relaxation is presented over the same extended time periods as the stress relaxation. Based on this, we show that no quasi-static balance exists between link tensions and bead diffusion that predicted in the work of Grassia & Hinch (1996). The intermediate-time behavior of the relaxation for a flexible molecule is shown to reappear as the early-time behavior for any semiflexible polymer; thus it constitutes a truly universal behavior for any (initially straight) polymer up to the ultra-stiff limit. Our numerical results compare well with experimental findings from initially straight single tethered DNA molecules.

Wednesday 4:25 Grand Station III BR7

On the coarse-graining of DNA and other polymers into bead-spring chains

Patrick T. Underhill and Patrick Doyle
Chemical Engineering, MIT, Cambridge, MA

The ability to use fluorescence videomicroscopy and optical tweezers to observe the behavior of single DNA chains has allowed for detailed comparison with molecular models. In particular, bead-spring chains have been used extensively to represent the worm-like chain behavior. These bead-spring chains are an attempt to coarse-grain out the fine details of the polymer while retaining the important "entropic restoring force." We have used both statistical mechanics and Brownian dynamics simulations to investigate, in a systematic manner, the behavior of bead-spring chains at different levels of coarse-graining. We studied both the force-extension behavior (how much the chain extends under an applied force) and the rheological behavior. The important dimensionless groups were identified, and the accuracy of the coarse-graining was found to depend strongly on the number of persistence lengths represented by each spring. We also showed the proper use and limitations of a "correction-factor" that has been used to improve the accuracy of the models. The general framework has also been used to analyze the behavior of the FENE and Fraenkel models. In this way, we can compare and contrast the behavior of DNA and synthetic polymers.

Wednesday 4:50 Grand Station III BR8

Stress and configuration relaxation of initially straight stiff polymers

Panagiotis Dimitrakopoulos and Inuka D. Dissanayake
Department of Chemical Engineering, University of Maryland, College Park, MD 20742-2111

This talk considers the relaxation of a single stiff polymer chain from an initial straight configuration in a viscous solvent. Examples of stiff polymers include biopolymers such as actin filaments, microtubules and rod-like viruses, as well as a host of stiff synthetic polymers such as Kevlar and polyesters. Physically this problem may correspond to the case of a polymer chain fully stretched by an (infinitely) strong flow and then relaxed by switching the flow off. As it is well known, large stresses are developed even in dilute polymer solutions involving fully stretched polymer chains. This problem is also motivated by recent experiments with single biomolecules relaxing after being fully extended by applied forces.

To study this problem, Brownian Dynamics simulations based on a discretized version of the wormlike model are employed. The relaxation of the full stress tensor is presented over a broad range of time scales, polymer lengths and chain stiffness. For the first time the configuration relaxation is presented over the same extended time periods as the stress relaxation; this is achieved by employing proper conformational functions and applying appropriate scaling laws. Based on this coupling, the polymer relaxation is shown to have two intermediate-time behaviors; an explanation for this finding is provided. The early intermediate-time behavior is shown to constitute a truly universal behavior for any polymer from the flexible up to the ultra-stiff limit.

Wednesday 5:15 Grand Station III BR9

Transition from flow-aligning to buckling in shear flows of dilute semiflexible polymers

Matteo Pasquali[1], Chris Wiggins[2], and Alberto Montesi[1]
[1]Department of Chemical Engineering, Rice University, Houston, TX 77005; [2]Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027

In a shear flow, Brownian rods flow-align and episodically tumble; flexible coils deform in the flow direction and undergo a Yo-Yo motion. We show that semiflexible dilute Brownian rods transition from flow aligning to buckling as the shear rate is increased. The transition is accompanied by a change of slope in the relationship between the viscosity and the shear rate. The onset of such transition can be predicted by linearizing the equations of motion of a semiflexible chain and projecting them onto bending modes (biharmonic functions). The linearized analysis yields the onset of buckling; however, because semiflexible rods tumble from the compression quadrant to the extension quadrant as they start buckling, the finite-time nature of the instability must be considered, and the amplitude of the perturbation at the beginning of the instability controls whether or not the semiflexible rods buckle considerably before escaping from the region of compression. We show that the finite amplitude of the instability is related to the equilibrium amplitude of the bending modes, which is dictated by equipartition of energy and depends on the competition of bending stiffness and thermal fluctuations. By combining the linearized analysis and the calculation

of the finite amplitude of the perturbation, we determine a phase diagram of buckling Brownian rods in shear flow, where the two relevant dimensionless numbers are the Weissenberg number and the ratio of persistence length to length of the semiflexible rod. We show that the analytical criterion agrees well with the results obtained from Brownian Dynamics simulations of semiflexible rods in shear flow.

Symposium EA
Entangled Polymers and Analytical Rheology

Organizers: Monty Shaw and James P. Oberhauser

Wednesday 1:30 Grand Station IV EA19

Theoretical modeling of the conformation of entangled linear polymers under rapid flow as measured by small angle neutron scattering

Richard S. Graham[1], Alexei E. Likhtman[1], Tom C. McLeish[1], Timothy M. Nicholson[2], Daniel J. Read[3], and Oliver G. Harlen[3]

[1]Polymer IRC, University of Leeds, Leeds, West Yorkshire LS2 9JT, United Kingdom; [2]Division of Chemical Engineering, University of Queensland, Queensland 4072, Australia; [3]Department of Applied Mathematics, University of Leeds, Leeds, West Yorkshire LS2 9JT, United Kingdom

Modern approaches to deriving constitutive equations for entangled polymer melts often involve theories for the dynamics of chain trajectories under strong flow. From knowledge of these trajectories the mechanical stress tensor can be predicted. However, the stress tensor is a relatively indirect probe of the chain conformation since it depends only on an average over many length-scales. Recent experiments performing small angle neutron scattering from entangled polymer melts have provided data for the single chain structure factor under strong deformation through and abrupt contraction. This measurement provides details of the chain conformation over a wide range of length-scales. In this paper we use a recently derived molecular theory [1] that predicts chain conformation down to the tube diameter length-scale we directly compare data and predictions for the variation of chain configuration of a polymer melt passing through an abrupt contraction. The theory successfully captures the variation of the degree of anisotropy with length-scale as a result of the deformation and the relaxation of this anisotropy after the contraction.

[1] RS Graham, AE Likhtman, TCB McLeish, ST Milner, Microscopic theory of linear, entangled chains under rapid deformation including chain stretch and convective constraint release, Journal of Rheology (submitted).

Wednesday 1:55 Grand Station IV EA20

Predicting the viscosity of a miscible polymer blend

Timothy P. Lodge and Jeffrey C. Haley

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

The composition-dependent viscosity of binary polymer mixtures has been a topic of interest for decades. Many empirical and semi-empirical “mixing rules” have been proposed, but a successful procedure based solely on molecular models has yet to emerge. The development of reptation-based treatments, incorporating additional effects such as double reptation, constraint release, and contour length fluctuations, has made it possible to describe accurately the linear viscoelastic properties of single component melts, and therefore the associated viscosities. Upon mixing two chemically distinct components, these treatments of chain dynamics can be modified to account for changes in, e.g., entanglement density and constraint release. However, the most important new ingredients are the distinct composition and temperature dependences of the component friction factors. These, in turn, can be anticipated on the basis of the respective self-concentrations, which are determined primarily by the persistence lengths. We demonstrate how this approach can anticipate all the various kinds of observed log viscosity versus composition behavior, e.g. concave up, concave down, linear, and “oscillatory”. We also assess the ability of this approach to make quantitative predictions.

Wednesday 2:20 Grand Station IV EA21

Predicting rheological behavior of polymer melts using a coupled relaxation mode model

Bangwu Jiang, Prajakta A. Kamerkar, David J. Keffer, and Brian J. Edwards
Department of Chemical Engineering, The University of Tennessee, Knoxville, TN 37996

Although it is tacitly understood that polymer solutions, melts, and blends exhibit a spectrum of relaxation times in simple experiments, most models for these materials quantify only one or two relaxation modes. Thus the fact that these models fail to describe the rheological properties of these materials in most applied flow fields is expected. An alternative class of models, in either integral of differential form, does incorporate multiple relaxation modes, but it treats the relaxation modes as uncoupled; i.e., the various modes have no effect on each other. Qualitatively, not to mention quantitatively, these models show no improvement over their single-mode counterparts. Recently, researchers have begun consideration of models involving coupled multiple relaxation modes, and these are showing substantial qualitative and quantitative improvement over previous models. In this presentation, we examine the simplest form of a coupled relaxation modes model, as derived through the methodology of nonequilibrium thermodynamics. Using a reasonable number of relaxation modes, the model parameters are fit to a limited amount of experimental data, namely, the storage and loss moduli of linear viscoelasticity, and the steady-state shear viscosity curve. Predictions are then generated for this set of parameter values that match experimental data for the steady-state first normal stress difference, transient shear stress and first normal stress difference, and transient uniaxial elongational viscosity at various strain rates.

Wednesday 2:45 Grand Station IV EA22

Linear melt rheology of Cayley trees, combs and star-combs

Dimitris Vlassopoulos[1], Michael Kapnistos[1], Jacques Roovers[2], Ioanna Halary[3], Nikos Hadjichristidis[3], and Richard J. Blackwell[4]
[1]Institute of Electronic Structure & Laser, FORTH, Heraklion, Crete 71110, Greece; [2]Institute for Chemical Process and Environmental Technology, NRC, Ottawa, Ontario K1A 0R6, Canada; [3]Department of Chemistry, University of Athens, Athens 15771, Greece; [4]DAMTP, University of Cambridge, Cambridge CB3 9EW, United Kingdom

We present a progress report on a long-term project aimed at elucidating the relaxation mechanisms of architecturally complex macromolecules. In particular, we present linear rheological data on series of well-defined nearly monodisperse branched polymers (polystyrenes, polybutadienes and polyisoprenes) of the Cayley-tree, comb and star-comb types. With the aid of recent tube-model theories we discuss quantitatively the complex relaxation of these systems in terms of hierarchical motions. By comparing with their linear counterparts we demonstrate the possibilities of altering the rheology of polymeric systems by introducing branches. Based on these results we also show that it is possible to analyze the viscoelastic response of telechelic polymers forming dendritic supramolecular structures in the melt.

Wednesday 3:35 Grand Station IV EA23

Linear and nonlinear relaxation dynamics of entangled branched polymers

Juliani Juliani[1] and Lynden A. Archer[2]
[1]Cornell University, Ithaca, NY; [2]School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853

Linear and nonlinear viscoelastic properties of model A3-A-A3 branched 1,4-polybutadiene melts and solutions are investigated experimentally, using mechanical rheometry and optical polarimetry, and theoretically using a recent theory for stress relaxation of entangled H-shaped polymers. This study provides experimental guidance on two key assumptions used in the theory. Namely, that stress relaxation of multiply branched, entangled polymers is hierarchical, and that relaxed portions of a branched molecule accelerate stress relaxation of unrelaxed sections of the same molecule in qualitatively the same manner as a low molecular weight diluent. Experimental results for multiarm polymer melts and solutions covering a broad range of arm and connector molecular weights provide support for a hierarchical relaxation process, but strongly disagree with the second assumption. Specifically, we find that while the damping function of entangled branched polymers at high strains and long times is consistent with theoretical predictions for entangled linear molecules, relaxed arms provide a much greater than expected retardation of branch point motion even on timescales well beyond the arm relaxation time. Branch point diffusivities estimated from the experimental data are typically one to two orders of magnitude lower than predicted by theory. The theory also underpredicts the breadth and amplitude of the dynamic storage and loss moduli of multiarm melts and solutions, particularly for materials where the number of entanglements per arm is low. Procedures for removing these discrepancies between theory and experiments are discussed.

Wednesday 4:00 Grand Station IV EA24

The effect of polydispersity on the rheology of branched polymer melts using the "hierarchical model"

Seung Joon Park and Ronald G. Larson
Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48105

A "hierarchical algorithm", which generalizes the Milner-McLeish theory, was developed to predict the linear viscoelastic properties of general mixtures of branched polymers. While its predictions are in reasonably good agreement with experimental data and illustrate how information on branching can be inferred from rheology, the model needs to be more quantitative. The original hierarchical model did not consider early-time fluctuations and needs an additional fitting parameter, which is the time constant in the prefactor of the expression for late-time fluctuations. In this work we develop a modification to the hierarchical model, which includes the early-time fluctuations and does not need the additional parameter, and compare its prediction with experimental data for polybutadienes and polyisoprenes. In the case of branched polymers, polydispersity affects the relaxation behavior more strongly because the arm relaxation time is exponentially dependent on the arm molecular weight. Thus, the small levels of polydispersity normally obtained in anionic polymerization can change the relaxation behavior drastically. We show how polydispersity in overall molecular weight and in the branch molecular weight affects the rheological properties of branched polymers.

Wednesday 4:25 Grand Station IV EA25

Hyperbranched polymer rheology

Jeffrey M. Pristera[1], Ralph H. Colby[1], Tim Long[2], and Serkan Unal[2]
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[2]Virginia Tech, Blacksburg, VA

Hyperbranched poly(ether ester)s were prepared by condensation polymerization from poly(ethylene glycol)s. The chain length between branch points is varied by utilizing different precursor chain lengths. The molar mass distributions are fitted well by a power law with exponential cutoff as predicted by Flory, assuming no cyclization. Steady and oscillatory shear rheology of these polymers will be discussed, with particular attention to the entanglement onset for hyperbranched polymers.

Wednesday 4:50 Grand Station IV EA26

An examination of entangled star polymers under shear flow using birefringence

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Star polymers have a single branch point and thus understanding the dynamics is a useful first step in gaining understanding of the more complicated, multiply branched polymers that are used in processing today. In the linear viscoelastic regime, the single branch point has already been demonstrated to have a huge effect in 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 a dominant relaxation mechanism. Convective constraint release will also be significant for star polymers, and it is expected that this will mitigate the differences between linear and star polymers once high enough shear rates have been reached. Measurements obtained with two color flow birefringence of the stress during startup and cessation of flow, along with steady state flow will be presented for both four arm stars and linear polymers with the same span molecular weight. These results will be compared with both a model that has been shown effective for linear polymers, and a simple model for stars under steady shear.

Wednesday 5:15 Grand Station IV EA27

Effects of polydispersity and branch-point motion on the rheology of entangled polymers

Sachin Shanbhag and Ronald G. Larson
Chemical Engineering, University of Michigan, Ann Arbor, Ann Arbor, MI 48109

Using a slip link description, which views entanglements between chains in a melt as slip links, we predict the linear viscoelastic behavior in some model polymer architectures including asymmetric stars and H-polymers for which branch-point motion is important. Current analytical treatments overpredict the mobility of the branch point in such architectures, and arbitrary corrections have to be applied to slow down this motion to reconcile theory and experiment. The slip link model offers insight into the drawbacks of the current analytical theory, in which the mobility of the branch point is set by the first passage time in a dilating tube. Analysis using the slip link model suggests substituting for the first-passage time in a dilating tube the first passage time in a fixed tube instead, for computation of the branch-point mobility. We also explore the issue of polydispersity and find that while it has only a small influence on the stress relaxation of symmetric stars for which the motion of the branch point is dynamically unimportant, it has a large effect on the stress relaxation of H-polymers.

Symposium LC
Liquid Crystalline Polymers and Self-Assembling Fluids

Organizers: Karen Winey and Peter Olmsted

Wednesday 1:30 Grand Station V LC10

Rheology of multi-component rod-like micellar solutions

Paloma Pimenta[1], Joan Gambogi[2], and Eugene Pashkovski[2]
[1]Chemical & Biochemical Engineering, Rutgers University, Piscataway, NJ; [2]Innovation and Strategy, Colgate-Palmolive Co., Piscataway, NJ

Relatively simple rod-like micellar systems can display very rich and complex rheological behavior. These systems can contain a single surfactant and a salt, for instance, cetyltrimethyl ammonium bromide (CTAB) and sodium salt of salicylic acid (NaSal). The linear rheology of CTAB-NaSal solutions is described in terms of Maxwellian model with the relaxation time τ_M depending on micellar reptation and scission. In the non-linear regime, the Newtonian flow is observed at shear rates below $1/\tau_M$; at higher shear rates, the stress plateau is observed. The dynamic model proposed by G. Marrucci and G. Ianniruberto. (Macromol. Symp., 1997, v.117, 233) accounts for the stress plateau in entangled systems via the Convection Constraint Release (CCR) mechanism.

The behavior of multi-component anionic surfactant systems, (Sodium Dodecyl Sulphate + Betaine + NaCl) is even more intriguing. In the linear regime, we have found that the elastic modulus increases monotonically with the addition of salts, even if the reptation time decreases. In the non-linear regime, we see significant deviations from the CCR model. In order to interpret these differences, we use rheology, rheo-optics and Diffusing Wave Spectroscopy.

Wednesday 1:55 Grand Station V LC11

Unusually slow reheal of rheology and structure in some viscoelastic micellar fluids

Gokul C. Kalur and Srinivasa R. Raghavan
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The central question that we explore in this study is: what happens to a sheared micellar fluid after the flow is stopped? Does the fluid “reheal” to its original (at-rest) rheology and structure rapidly, or slowly? For example, do shear-aligned micelles revert quickly to an isotropic state, or do they persist in an aligned configuration for a long period of time? Are the steady and dynamic rheological properties measured immediately after vigorous shear identical to those of an unsheared sample? We have studied the post-shear reheal behavior of a wide range of viscoelastic wormlike micellar fluids composed of different surfactants. In this talk, we will focus on two peculiar instances where the sample reheal is unusually slow. In one case, the post-shear elastic modulus (G') takes more than 10 min to revert to its initial value, even though the sample's viscoelastic relaxation time is only a few seconds.

In a second case, while the rheology recovers quickly following shear, we find through flow-birefringence studies that the micellar chains are trapped in an aligned state for a long period of time (several hours). Thus, the latter sample appears to show a shear-induced structural transition from micelle to liquid crystal even though the bulk rheology has rehealed. We are investigating these phenomena through a combination of rheology, rheo-optics, small-angle neutron scattering under flow (FSANS), and optical microscopy under shear. Possible microstructural interpretations for these experimental findings will be offered.

Wednesday 2:20 Grand Station V LC12

The microstructure and rheology of mixed cationic/anionic wormlike micelles

Beth A. Schubert, Norman J. Wagner, and Eric W. Kaler
Chemical Engineering, University of Delaware, Newark, DE 19716

Wormlike micelle solutions exhibit viscoelastic shear rheology with important technological applications. Cationic and anionic surfactants can self-assemble into worm-like micellar solutions, where the microstructure is tunable through concentration, composition, and by the addition of simple electrolytes or penetrating electrolytes. Consequently, such mixed surfactant systems afford a broad range of rheological properties that can be controlled through multiple routes, making them attractive for formulations. However, the relationships between chemical composition, solution microstructure, and solution rheology are poorly understood for mixed ionic surfactant micellar solutions. Here, the rheology, flow-birefringence, and small angle neutron scattering of model, mixed cationic/anionic wormlike micellar solutions composed of cetyl trimethylammonium tosylate (CTAT) and sodium dodecyl benzyl sulfonate (SDBS) are studied over a broad range of solution compositions. This combination of experimental techniques enables independent determination of the self-assembled microstructure (persistence, entanglement, interaction, and contour lengths) that governs the rheological properties. Comparison of the effects of a hydrotropic salt (NaTosylate) and of a screening electrolyte (NaCl) illustrates the influence of micellar charge on the persistence length, and hence, the microstructure and rheology. Surfactant concentration, mixing ratio, and electrolyte concentration and composition systematically affect the self-assembled microstructure such that a transition in rheology from that of nonionic wormlike micelles to that of polyelectrolytes can be spanned. The experimental results are placed within the framework of existing theories for the growth of charged micelles, with the resulting micellar microstructure resulting from a balance between the endcap, electrostatic and branching energies. These results provide a framework for establishing structure-property relationships for this class of micellar fluids.

Wednesday 2:45 Grand Station V LC13

Stepping at steady state: The kinetics of onion formation

Georgina M. Wilkins and Peter D. Olmsted
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The kinetics of the shear induced formation of multi-lamellar vesicles (MLV's) from a lamellar phase is reported for a quaternary mixture of sodium dodecyl sulphate (SDS), water, pentanol, and dodecane. The rheological steady state behaviour exhibits a discontinuity from which we infer a change in microstructure. At intermediate stresses, the behaviour appears to be history dependent with long times to reach steady state; we interpret this range of stresses in terms of the coexistence of lamellae and MLV's. The stress jump experiments show two widely separated times to reach steady state, suggesting an evolution of two coexisting states. We study the kinetics of the formation of the intermediate state, and the evolution of the state under jumps in the stress. The transient stress creep behaviour shows either one or two shear thickening events as a function of time, depending on the applied stress. The effects of different start-up procedures are also investigated.

Wednesday 3:35 Grand Station V LC14

Effect of complex flow kinematics on the molecular orientation distribution in injection molding of liquid crystalline copolyesters

Wesley Burghardt[1], Stanley Rendon[1], and Robert Bubeck[2]
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Properties of liquid crystalline polymers (LCPs) depend critically on the molecular orientation distribution, which in turn can be dramatically influenced by flow fields during processing. Our group has developed in situ x-ray scattering methods to measure orientation distributions in steady, isothermal complex channel flows of LCPs. We find that complex orientation states arise from the competition of inhomogeneous shear and extension. Here we consider the extent to which these concepts translate to the more difficult transient & nonisothermal case of injection molding, through ex situ studies of molecular orientation distributions in injection molded plaques. These studies employ a new, low-cost aromatic copolyester based on the mesogen dihydroxy-α-methylstilbene. In comparing behavior in molded plaques against in situ studies of the same material in isothermal channel flows, we find strong similarities in the type of orientation states observed. Further, systematic changes in the relative importance of shear and extension through changes in the plaque thickness lead to changes in orientation distribution that would be anticipated from our evolving understanding of the effect of mixed shear and extensional flows on orientation. These results verify that idealized isothermal studies not only elucidate fundamental flow/orientation relations, but also serve as a useful intermediate step towards understanding true processing conditions.

Wednesday 4:00 Grand Station V LC15

Continuous preparation and characterisation of thermoplastic/carbon nanotube composites

Carlos A. Bernardo[1], José A. Covas[1], Olga S. Carneiro[1], João M. Maia[1], Ferrie W. van Hattum[1], Imre Kiricsi[2], Lazslo Biró[3], and Z Horvath[3]
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The main aim of the present work is the continuous production of polymer/carbon nanotube composites a view to making new materials with interesting properties and assessing the feasibility of scaling-up production techniques. The composites were characterized at two different levels. At the nanoscale, they were studied by both atomic force and transmission electron microscopies. At the macroscopic scale, the composites were characterized in terms of their rheological, mechanical and electrical properties. Initial results indicate that there is strong mechanical and electric reinforcement for nanotube concentrations in excess of approximately 2%(w/w), even though the dispersive mixing achieved is not particularly good. Integration of the experimental information from both the nano and macroscales with production data will allow the establishment of a procedure to make high-performance composites.

Wednesday 4:25 Grand Station V LC16

Lyotropic nematic dispersions of single-walled carbon nanotubes in strong acids

Virginia A. Davis, Nicholas G. Parra-Vasquez, Lars M. Ericson, and Matteo Pasquali
Chemical Engineering, Rice University, Houston, TX 77005

Single-walled carbon nanotubes (SWNTs) have been dispersed successfully in strong acids (e.g., sulfuric) at high concentration (up to 10% by volume). Rheology and microscopy show that SWNTs in strong acids parallel the phase behavior of rigid rod polymer solutions used to produce high performance fibers such as Kevlar. As the concentration of SWNTs in acid is increased, the system transitions from an isotropic phase at exceedingly low concentration (approximately below 100 ppm vol), to a biphasic phase formed of spaghetti-like supramolecular aggregates of mobile SWNTs intercalated by acid layers, to a fully liquid crystalline phase characterized by a polydomain structure. Liquid crystallinity is evidenced by birefringence in the absence of shearing, formation of aligned species (alewives) upon phase-separation induced by the introduction of water, and rheological signatures such as a non-monotonic relationship between viscosity and concentration, a first normal stress difference that changes sign with increasing shear rate, and long oscillatory transients. Highly aligned macroscopic fibers can be spun from good-quality dispersions simply by extruding the SWNT/acid dispersion into a stationary ether bath. The fiber show a ~20 to 1 ratio of parallel to perpendicular Raman signal and are quite dense (~80%) even in the absence of drawing.

Wednesday 4:50 Grand Station V LC17

Shear rheology of a hydroxypropylcellulose melt in the anisotropic and isotropic states

Eric S. Scribben[1], Donald G. Baird[1], and Thomas S. Wilson[2]
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Hydroxypropylcellulose (HPC) is used as a model thermotropic liquid crystalline polymer system because of the ability to reach the clearing point at a temperature before any significant degradation occurs. Initially, a detailed set of structural studies (e.g. WAXS, DSC, light scattering, and optical microscopy) were carried out to identify the structure present and the transition temperatures for a HPC melt. In particular, the HPC system in the anisotropic state contained primarily liquid crystalline (LC) phase and low levels of crystallites and isotropic phase. It was observed that in the isotropic state the transient stress growth and relaxation response resembled typical isotropic melts. For example, the peak stresses varied with shear rate but reached a maximum at a similar strain and the primary normal stress difference was positive. In the anisotropic state the peak stress also occurred at a similar strain and the peak was independent of shear rate in agreement with behavior observed for other LCP's. The apparent negative values of N1 appeared to be related to the presence of a yield stress and hence residual stresses which lead to baseline errors (initial zero setting). The Doi theory predicted reasonably well the stress growth behavior of the anisotropic state when a multi-domain averaging of the stress tensor was used.

Wednesday 5:15 Grand Station V LC18

Effect of high electric fields on the isotropic phase of a lyotropic liquid crystalline system

Todd J. Menna and Frank E. Filisko
Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

PHIC is a well-known lyotropic liquid crystalline polymer, capable of exhibiting isotropic, biphasic, and nematic phase domains over wide concentrations. Morphological and rheological studies of the PHIC were done under high AC electric fields at various frequencies, and methods were developed for characterization of the isotropic materials response through relation to the optical Kerr effect. The morphological studies, which included birefringence measurements under shear and high fields, were performed on a custom constructed inverted stage microscope arrangement. The rheological studies were performed on rheometers modified for high electric field studies. The Kerr effect transitions within the material are currently being investigated as a means of describing the inherent increase in material strength and viscosity with increasing applied field. Due to the structure of the phase itself, biphasic solutions have been found to exhibit behaviors similar to those of the isotropic and nematic phases and research is being conducted as a means of relating this response to the rheological properties of the solution.

Thursday Morning

Symposium SM
Suspension and Multiphase Fluids

Organizers: Andy Kraynik and Michael Solomon

Thursday 8:05 Grand Station I SM42

Rheology of highly concentrated particle-liquid systems

Ronnie G. Morgan and Jeffrey F. Morris
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A number of industrial applications employ suspensions of non-colloidal particles in viscoelastic non-Newtonian carrier fluids, such as those employed in hydraulic fracturing of oil and gas wells. In this application, typical carrier fluids are high molecular weight polymer systems, such as cross-linked guar solutions, which exhibit viscoelastic properties. The viscoelasticity is believed to be important for effective transport and placement of particles within hydraulic fractures, but the role of elastic normal stresses on friction loss and particle transport is not well understood. This is especially true for solids-laden systems. Most published work on normal stresses in such materials involves rotational rheometry with cone-plate or plate-plate sensors operating under low shear rate and/or low strain oscillatory conditions; operational difficulties such as retention of the material within the shearing gap often limit both the shear rate range and accuracy of stress measurements. As a result, little information is available on the normal stress effects of particle laden viscoelastic fluids. This work focuses on employing extrusion rheometry and jet swell measurements to characterize the viscoelastic properties of particle laden fluids. Thin "slot dies" and circular dies of different sizes and lengths are employed to provide a wide range of relaxation times and shear rates. Small strain oscillatory rheological data are collected on the liquid without solids with a rotational rheometer, and compared with jet swell data. Relaxation modulus and time dependent shear stress and normal stress difference material functions developed for cross-linked borated guar gum and particle concentrations from 0 to 0.6 by volume will be presented.

Thursday 8:30 Grand Station I SM43

Visco-elastic surfactant fluids as particle transport media for hydraulic fracturing operations

Phil F. Sullivan[1], Haiying Huang[2], and Erik Nelson[3]
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Hydraulic fracturing is an oilfield reservoir stimulation technique, where fractures are created by the injection of viscous slurry into the rock mass. The placement of solid particles props the fracture open and thus creates a conductive passage for the flow of hydrocarbons. The ability to transport particles is an important aspect of fluid design. It is desired to have defined rheological criteria for evaluating fluids. The "map" between fluid rheology and successful particle transport (i.e., ideally no settling during transport) is, however, not fully understood. Current practices with crosslinked polymer fluids assume power-law-like rheology models and consider apparent viscosities at given shear rates as an index. This conventional "rule-of-thumb" nevertheless does not appear to be valid for self-assembling visco-elastic surfactant (VES) fluids. To better understand the mechanisms of particle transport in VES fluids, laboratory-scale slot tests have been performed. The effects of temperature, flow rate, particle size, and slot geometry have been investigated. Results indicate that the onset of particle settling is associated with a critical temperature, which varies with all other factors. To account for this flow dependence on temperature, a new phenomenological model has been proposed. The analytical results agree qualitatively with experimental evidence and provide insights for rheological properties necessary for fluid design for particle transport in hydraulic fracturing treatments.

Thursday 8:55 Grand Station I SM44

Characterization of bauxite residue for neutralization of acid mine drainage

Elaine M. Humiston
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Bauxite Residue is a by-product of the alumina refining industry. Worldwide, the aluminum industry produces over 70 million metric tons of residues per year. The residue is currently stored at points of production. The material is highly alkaline, contains large amounts of silica, and can have many pollutants leach from the storage facilities. A number of different environmental problems as well as the issue of diminishing storage space has led the aluminum industry to investigate alternative uses for bauxite residue.

Another problem the aluminum industry faces is continued management of acid mine drainage from spent mines. Utilization of bauxite residue for neutralization of acidic waters could greatly reduce waste and environmental impact of the aluminum industry, as well as reduce costs for storage, acid mine drainage management, and potential ground water contamination to mention a few.

Rheological characterization and comparison of bauxite residue, and bauxite residue derivatives is an important step in the process of finding alternative uses for the material. A flat plate rheometer and a capillary rheometer are being used for this characterization. A range of volume fractions of solids and pH has been examined. Results from this investigation will be presented and discussed.

Thursday 9:20 Grand Station I SM45

Influence of filler-content on rheology of non-aqueous dispersions

Raghuram Gummaraju[1], Kurt Vance[2], and Heinz Plaumann[1]
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Upon incorporation of fillers, polymers could become non-Newtonian in nature and resemble non-aqueous dispersions. Such filled-polymer dispersions are extensively used in different polyurethane applications. Rheology of these polymers will facilitate understanding of inter-phase interactions and their influence on viscosity of these dispersions. In the current investigation, a technique using a SR-2000 model (Rheometrics) rheometer was implemented to analyze rheological behavior of non-Newtonian fluids. Two different polymers were utilized to illustrate different types of non-Newtonian behaviors, with respect to the dependence of their viscosities on applied shear-rate.

Rheological profiles indicated that filled-polymers, based on processing conditions, demonstrate either shear-thinning or shear-thinning followed by shear-thickening phenomena. Furthermore, these investigations showed that the viscosity profile of such a polymer is dependent on % filler-content. Also, a model that predicts % filler-content from a limited region of the viscosity profile has been developed. These predictions have been compared to % filler-content obtained using other techniques. These results show that the rheological investigations of polymers, incorporated with fillers, will help us comprehend the utility of such polymers within various polyurethane applications and the possible impact of non-Newtonian rheology on processing of these polymers.

Thursday 10:10 Grand Station I SM46

Rheological behavior of polystyrene (PS) with incorporation of hybrid polyhedral oligosilsesquioxane (POSS)

Jian Wu[1], Timothy S. Haddad[2], and Patrick T. Mather[1]
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We report the linear dynamic viscoelastic properties and nonlinear transient rheology of the linear thermoplastic non-polar hybrid inorganic-organic polymer: random copolymer of polystyrene (PS) and styryl-based polyhedral oligosilsesquioxane (POSS), $R_7(Si_8O_{12})$(Styryl), with R = isobutyl. A series of styrene-host copolymers with 0, 6, 30 wt% POSS were investigated. Rheological measurements have shown that incorporation of POSS has a great influence on the polymer viscoelastic properties. Specifically, with increasing POSS content, the rubbery plateau modulus dramatically decreases, suggesting a strong influence isobutyl-POSS sidegroups on entanglement density. We also observe a plasticization effect of isobutyl-POSS groups as reflected in decreasing glass transition temperature with increasing POSS content. Meanwhile, interchain interactions between the highly functionalized (R_7) POSS groups results in a retardation of polymer chain motion, broadening the rubbery plateau to lower frequencies/longer times. This mechanism can be explained by "sticky reptation" model developed by Leibler et al [Macromolecules, 24, 4701 (1991)] for hydrogen-bonded linear chains. Finally, intermittent shear flow experiments have revealed that POSS copolymers show a stronger dependence of stress growth trace on the period of rest after cessation of steady shear flow than pure polystyrene. This observation indicates that interactions between POSS groups, perhaps in the form of nanostructured domains, breaks during shear start-up, but rebuilds during rest after cessation of steady shear flow.

Thursday 10:35 Grand Station I SM47

Morphological effects of tethered and untethered polyhedral oligosilsesquioxanes (POSS) on the viscometric and linear viscoelastic properties of PMMA

Edward T. Kopesky[1], Gareth H. McKinley[2], Robert E. Cohen[1], and Timothy S. Haddad[3]
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Polyhedral oligosilsesquioxanes (POSS), hybrid organic-inorganic molecular composites with structure $R_xSi_xO_{1.5x}$, have shown promise in engineering plastics due to their enhancement of the thermal stability and abrasion resistance of soft materials without substantially increasing their viscosity. However, little is known about the effect POSS has on the viscometric properties of thermoplastics in the melt state. In this study, PMMA blended with - and copolymerized with - two distinct POSS molecules ($R_8Si_8O_{12}$) containing isobutyl and cyclopentyl R-groups, respectively, was tested in steady shear flow. Three specific systems were analyzed: PMMA homopolymer (M_w = 140,000 g/mol) blended with low volume fractions of discrete POSS particles, MMA copolymerized with propylmethacryl-POSS (M_w = 310,000 g/mol), and the PMMA-POSS copolymer blended with POSS particles, to contrast the effect of tethered versus untethered POSS moieties on the polymer's rheological properties. The morphologies of each sample were characterized using X-ray diffraction and the scattering patterns are related to the rheological properties measured in steady shear and in small amplitude oscillatory shear. The change in zero shear-rate viscosity with volume fraction is notably different from what is observed using conventional macroscopic fillers. We also observed a strong time dependence of the storage and loss moduli at low frequencies for the PMMA-POSS copolymers due to structure development amongst the tethered POSS molecules. These results are compared with previously reported studies of POSS systems, and the scaling of the observed results with volume fraction is compared with predictions from percolation theory.

Thursday 11:00 Grand Station I SM48

Rheology of polyamide-6/clay based layered silicate nanocomposites

Ravishankar K. Ayyer and Arkady I. Leonov
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This study analyzes the melt state rheological properties of layered silicate nanocomposites based on polyamide-6 and montmorillonite. A set of simple shearing experiments at two different temperatures was carried out for both the neat polyamide-6 (PA-6) and nano-clay dispersed polymer system. The study includes the transient start up shear flow followed by stress relaxation after cessation of steady flow and dynamic experiments. The oscillatory shear behavior of the nanocomposite differs markedly from that of the neat PA-6 matrix. For the system under study thermal stability of the polymer matrix posed many restrictions on their rheological study. Hence through directed efforts which included rheological as well as thermal studies of the materials, an experimental window was established wherein the polymer matrix was confirmed to be thermally stable. Additionally, the relaxation spectra for both the neat and filled polymer systems were obtained from the dynamic oscillatory measurements using the Pade-Laplace procedure. Extra Maxwellian modes observed in the case of nanocomposites relative to the neat polymer are attributed to the particle network formation above percolation threshold in the nanocomposite.

Thursday 11:25 Grand Station I SM49

Rheo-dielectric studies of the aggregation of submicron TiO_2 suspended in polyethylene

Tian Hao and Richard E. Riman

Ceramic & Materials Engineering, Rutgers University, Piscataway, NJ 08854-806

Rheological and rheo-dielectric properties (Rheometrics ARES-DETA system) were investigated for suspensions composed of submicron TiO_2 (weight moment median size around 230nm) coated with organic species and low molecular weight polyethylene. The dielectric properties of the suspensions were studied under an oscillatory mechanical field for the purpose of extracting microstructure and particle aggregation information. Comparison was made between the submicron TiO_2 samples with and without organic coating on the surface. The established theories between particle microstructure and dielectric properties were used to analyze the dielectric data for the interfacial polarization process. It was found that the coated TiO_2/polyethylene suspension shows a lower dielectric constant and a lower viscosity than uncoated one. The coated TiO_2 particles form a relative ordered microstructure, so the dielectric and mechanical loss tangent is lower than that of uncoated sample. Particle aggregation and agglomeration resulted microstructure are ascribed to such differences.

Thursday 11:50 Grand Station I SM50

The effect of hydrodynamic interactions on the kinetics of ternary mixtures with reversible chemical reactions

Kevin Good[1], Olga Kuksenok[2], Gavin Buxton[2], Valeriy V. Ginzburg[3], and Anna Balazs[2]

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We investigate the structural evolution of an A/B/C ternary mixture in which the A and B components can undergo reversible chemical reaction and form the C component. The morphology of the system is described in terms of two order parameters: the first order parameter is the difference in the density of the A and B components, and the second order parameter represents the density of the C component. We assume that the mixture is incompressible. The free energy for the mixture is formulated based on previous work for the two-order parameter systems (see Komura, Kodama, PRE, 55, (1997)) with the appropriate modifications for reactive systems. The evolution of each order parameter in time is described by a Cahn-Hillard equation with an advection term. The velocity field obeys the Navies-Stokes equation. We adopt a lattice Boltzmann model to simulate the evolution of the above ternary fluids. The C component acts like a surfactant and is localized mostly on the interface between the A and B components; the presence of C leads to the lower interfacial tension between the A and B.

We analyzed the growth of the A/B domain versus different reaction rates for the fluid in the diffusive and viscous regimes. For each of the above cases, we also analyzed the saturation of the interface by the C component. In the diffusive regime, even for the case where forward and backward reaction rates are equal, the formation of C on the interface completely stops the domain growth. The steady state value of the domain size is defined by the reaction rate. For the fluid in viscous regime, the A/B domain growth is slowed down by the formation of C on the interface but does not stop for the case of equal reaction rates of the forward and backward reactions. We found that in order to further slow down or to stop A/B domain growth in a viscous regime, the forward reaction rate should be significantly higher than a backward reaction.

Symposium BR
Biorheology

Organizers: Robert Armstrong and Patrick Doyle

Thursday 8:05 Grand Station III BR10

Kinetics of helix reversion and physical gelation of gelatin

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The helix reversion of gelatin is monitored using optical rotation following a temperature quench. We find that the helix reversion has a combination of first-order and second-order kinetics. This makes the critical nucleus a two-stranded helix, in contrast to the single-stranded nucleus assumed in the Flory-Weaver model. A simple kinetics model allows estimation of the temperature dependence of the stable helix length. Rheo-optics is then used to study the gelation that results from helix reversion. Viscosity data below the gel point were used to evaluate the gel point and the viscosity exponent of percolation theory. Above the gel point, creep-recovery experiments are used to measure the shear modulus and determine the percolation modulus exponent. During gelation, the time-dependent optical rotation shows an initial rapid growth region where new helices are formed, followed by a slower growth region involving helix lengthening. For cases where the gel point occurs before the helix reversion slows appreciably, the viscosity and modulus exponents are found to depend on gelatin concentration, but not on temperature. However, anomalous exponents are measured using the same methods at higher temperatures, where the helix reversion slows appreciably below the gel point. The observed concentration dependences of the percolation exponents are discussed in terms of chain overlap and entanglement. A model for the kinetics of helix reversion is presented and gel times are predicted over the entire range of possible gelatin concentrations and temperatures. These predictions compare nicely with experimental data covering the ranges of gelatin concentration and temperature where measurements have been made.

Thursday 8:30 Grand Station III BR11

Evolution of microstructure and rheology in mixed biopolymer systems

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Synergistic biopolymer blends composed of xanthan and enzymatically-modified guar galactomannan are investigated in terms of their time-dependent properties. In particular, a side-chain cleaving enzyme, a-galactosidase, is used to cleave off galactose sugar units from guar to produce modified galactomannans with varying galactose contents of 25.2 and 16.2 % respectively. Confocal scanning laser microscopy (CSLM) and dynamic rheology are used to monitor the properties of each of these two modified guar gum in solution as well as in blends with xanthan as they are allowed to age over a period of three weeks. Our results indicate that solutions of guar with a higher galactose (25.2%) content undergo no rheological change over the period of observation and show a constant gel elastic modulus (G') in blends with xanthan. Confocal images of the solutions and the blends also indicate that the systems are stable over a period of three weeks. In contrast, guar gum with a lower galactose content (16.2%) forms interchain associations in solution developing aggregates that convert it from a macromolecular solution to a gel. This is reflected in its dynamic moduli which increase significantly with time and show a transition from frequency-dependent behavior with G'' (viscous modulus)>G' (elastic modulus) to a frequency-independent character with G'>G''. This process of association and phase separation is directly observed in confocal images of the modified guar as well as in its blend, though not to the same extent in the latter. The presence of a second component thus seems to retard the association process. Interestingly, the blend moduli remain unchanged in magnitude and show gel-like features even though the mode of association and concomitant microstructure changes.

Thursday 8:55 Grand Station III BR12

Rheology of hagfish mucins

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The Hagfish is an evolutionary throw-back, a jawless fish that parted company from the phylum Chordate before the appearance of true vertebrates. These relatively simple creatures have evolved a spectacular defence mechanism that involves the generation of large amounts of defensive slime. This complex system is excreted by the hagfish and almost immediately generates a space filling “gel” that is composed of associated mucins with a longer range structure imparted by long keratin-like fibers. Currently little work has been performed on studying the rheology of the slime itself, or the properties of the gelling mucins. Here we present shear rheology for the mucins with respect to concentration and consider the behavior of these glycoproteins in solutions relevant to natural conditions.

Thursday 9:20 Grand Station III BR13

Heart-valve mechanics: Elastic and viscoelastic

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Heart valves are complex structures that are often modeled as isotropic elastic membranes. In reality, they are complex, orthotropic, laminated structures whose response is predominantly nonlinear elastic, yet possesses viscoelastic attributes. With each heart beat, the valve extends to strains as high as forty percent, and supports stresses of several hundred kPa that rise from zero in less than 100 msec. During its lifespan, the valve opens and closes about three billion times. No synthetic material can match the unique combination of strength, compliance and durability of the native heart-valve tissue.

The Heart Valve Lab at the Cleveland Clinic is dedicated to the study of these structures. As an integral part of this group, our task is to better understand the role that viscoelasticity plays in healthy valves and, in time, diseased valves, too.

An orthotropic, finite-strain, nearly incompressible, elastic model has been derived from invariant theory that represents heart-valve response. It accounts for the fact that collagen fibers do not support compressive loads, and that there is splay in their alignment. Using this elastic model as our backbone, a K-BKZ viscoelastic model has been constructed. Two relaxation functions are being compared against experimental data: Fung's QLV (quasi-linear viscoelastic) kernel, and Caputo and Mainardi's FOV (fractional-order viscoelastic) kernel. Both functions are capable of describing almost rate-insensitive behavior, in accordance with experimental observations. Because the ideal experiments desired for material characterization cannot be achieved in practice, a direct fit method that accounts for the entire loading history has been employed to obtain material parameters, and has been found to yield superior results when contrasted with more conventional methods.

Thursday 10:10 Grand Station III BR14

Influence of hydrodynamic interactions on the coil-stretch transition of polymers in extensional and mixed flows

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In this work, we discuss the influence of hydrodynamic interactions (HI) on polymer dynamics in planar extensional and general mixed flows. The nature of the coil-stretch phase transition for polymers in extensional flow has been a long-standing problem in polymer physics. Using single molecule fluorescence microscopy, we examined very long DNA molecules (< 1 mm) in planar extensional flow and observed kinetically separated bistable polymer configurations at flow strengths slightly below the coil-stretch transition. For shorter-length DNA molecules (150 to 300 microns), we measured transient molecular extension at different flow strengths and did not observe configuration hysteresis. Using Brownian dynamics (BD) simulation, we model polymers as bead-spring chains and include intrachain HI through a Rotne-Prager interaction between beads. For long chain polymers, BD simulations show polymer configuration hysteresis in extensional flow. Polymer configurational energy landscapes determined from Brownian dynamics simulation exhibit a double-welled potential near the phase transition, giving rise to bistable polymer behavior. For BD simulations, we apply an algorithm developed in our research group (Somasi, *et al.*, *J. Non-Newtonian Fluid Mech.*, vol. 108, p. 227-255, 2002), and we report on our attempts at further algorithm development in increasing the efficiency of HI calculations. Finally, we will discuss the influence of HI on polymer dynamics in mixed flows using BD simulation. We examine the idea that for general three-dimensional mixed flows and for planar mixed flows in the extension-dominated regime, the coil-stretch transition should be first order.

Thursday 10:35 Grand Station III BR15

Molecular conformation of DNA in free-surface flows of dilute solutions

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Free surface flows arise when a flowing liquid layer meets another fluid to form an interface. Examples of flows with free surfaces can be found in a number of industrial applications (e.g., coating, spraying) as well as the biological sciences (e.g., DNA arrays). Many processes involve the use of dilute solutions of polymers in viscous solvents. The configuration of the polymer molecules is spatially inhomogeneous and difficult to calculate or measure; it is important because microstructural changes in flow influence the rheology of the solution and controls the efficacy of the process (as in spraying) and determine the properties of the final product (as in coating).

The deformation of single polymer molecules was investigated in a complex inhomogeneous free-surface flow. Individual DNA molecules in an ultra-dilute solution were observed with a fluorescence microscope, as they flow between a scaled-down rotating roll and a stationary glass knife. The roll picks up a thin layer of liquid from a pool and drags it to the knife, establishing a meniscus. At low roll speed recirculations are present under the glass bar. The mean fractional extension of polymer molecules varies in regions of different local Weissenberg Numbers. At the two menisci, no polymer distortion is observed.

At high roll speed, part of the entrained liquid is rejected by the knife and runs back toward the pool; two separation surfaces arise, upstream and downstream of the minimum gap between roll and knife. At the upstream surface the DNA stretches considerably in the plane of focus. At the downstream surface the DNA extends normal to the coverslip and contracts in the plane of focus. At the two free surfaces the molecules enter a nodular recirculation and flow axially.

A computational study of the flow is in progress; it is based on a Galerkin-Finite Element solution of the flow equations and on a Brownian Dynamics simulation of the conformational dynamics of the DNA molecules.

Thursday 11:00 Grand Station III BR16

Electrophoretic dynamics of large DNA stars

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We have developed a procedure for synthesizing large stable branched DNA structures that enables visualization via fluorescence microscopy. Using this procedure, we have synthesized large DNA stars and observed their electrophoretic behavior in polymer solutions and gels. Above the entanglement threshold for polymer solutions, the star arms extend and drag the core through the matrix during electrophoresis. In gels, where matrix entanglements are fixed, stars are trapped when entanglements with matrix molecules prevent the core from being pulled through the matrix. We have determined the mobility of four arm DNA stars and T2 dsDNA in dilute, semi-dilute, and entangled polymer solutions and compared the data to models found in the literature. Results for linear T2 dsDNA are in good agreement with the predicted pore size scaling of the biased reptation with fluctuations model (BRF) when the pore size is smaller than the Kuhn length of the analyte.

Thursday 11:25 Grand Station III BR17

Direct visualizations of polymer tumbling in steady shear flow

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We report the direct visualization of individual polymer molecules undergoing steady shear flow in a novel geometry that allowed observation in the flow-gradient plane. We probed polymer dynamics in dilute solutions including dimensionless shear rates (Weissenberg number = Wi = shear rate × longest polymer relaxation time) from 1.6 to 584 by using two sizes of DNA molecules — 22 μm and 80 μm. These polymers contain over 300 persistence lengths and therefore can be considered flexible. We measured power-law exponents of Wi for the decays of both the characteristic thickness of the configuration space in the gradient direction and the orientation angle of the configuration space relative to the flow direction. A –0.46 decay exponent for orientation was found over the entire range of Wi. Thus, polymer configuration space was found to become, on average, thinner (in the gradient direction) and more aligned with the flow direction as we increased the shear rate.

Three mechanisms for shear-induced, stretching transitions were found: recoil, restretch and tumble. The frequency of these events was extracted by inspection of the movies as the total number of events divided by the total experimental time. The end-over-end tumbling frequency apparently increased monotonically. Cross-correlations between thickness and extension fluctuations revealed a causal chain relationship leading to four phases of motion: thickening, stretching, aligning, and recoiling. Finally, we experimentally measured the power spectrum of the length auto-correlation for several values of Wi and found distinct peaks at low frequency signaling that the motion is weakly periodic. The resonant frequencies coincided with the independently determined tumbling frequencies. These findings were reproduced by Brownian Dynamics simulations using a multi-bead-spring model with a worm-like chain force law.

Thursday 11:50 Grand Station III BR18

Effect of molecular weight of polymer matrix on electrophoretic mobility of large linear and star shaped DNA

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It is known that the molecular weight of the matrix polymer chains plays an important role in determining the resolution of electrophoretic separation of polyelectrolytes in polymer solutions. To investigate the effect of polymer molecular weight on linear and branched analytes we have done a systematic study of electrophoretic mobility of large linear and branched DNA in dilute and semidilute polymer solutions. We have used monodisperse PEO in tris-borate-EDTA buffer as polymer matrix. The polymer solutions are characterized by their overlap concentrations (i.e. c^*). In the present study the range of concentrations from below c^* to ~$3c^*$ has been probed for the effect of matrix molecular weight. Measurements of steady-state center of mass velocity of both linear and star DNA in PEO solutions are taken using an intensified CCD camera and image processing software. We compared our experimental data with theoretical models for electrophoretic mobility in non-entangled and semi-entangled solutions.

Symposium ER
Extensional Rheology

Organizers: Monty Shaw and James P. Oberhauser

Thursday 8:05 Grand Station IV ER1

The use of capillary breakup extensional viscosity to examine concentration dependence of relaxation time

Gregory M. Neal and Gavin J. Braithwaite
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Recently there has been a growing interest in quantitative techniques for determining the extensional rheology of liquids. Although melts and concentrated solutions can be relatively easily characterized, dilute solutions have so far resisted robust analysis. The advent of techniques based on surface tension driven breakup of liquid bridges has allowed access to much lower viscosity solutions than previously allowed routinely. In this talk we study the dependence of relaxation time of a model aqueous system based on poly(ethylene oxide) in a poly (ethylene glycol)/water mix. These materials are easy to prepare, have relatively simple shear behaviors and can be prepared in a homologous series of molecular weights. They are thus ideal for examining the dependence of the relaxation time with both molecular weight and concentration.

Thursday 8:30 Grand Station IV ER2

Extensional rheology of paper coating colors at high strain rates

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Paper coating colors are aqueous suspensions composed mainly of mineral pigments, thickeners, binders, dispersing agents and other additives in solution. It is well-known that the rheological complexity of these systems is due to global interactions between their compounds. Coating colors are applied onto moving paper web for improving the optical and printing properties. Roll and jet coating are presently the most used technologies for paper coating at high speed. Coating colors are submitted to high strain in both roll or jet coaters, therefore extensional viscosity plays a major role in the process.

In this work, an orifice flowmeter was used for measuring the extensional properties of complex rheology fluids. The principle of this flowmeter is based on the pressure entry technique. The equipment was firstly calibrated in terms of a dimensionless Euler number as a function of the Reynolds number with Newtonians fluids. The calibration curve was then used to determine the apparent extensional viscosity of coating colors.

High concentrated coating colors based on paper formulations were made-down with delaminated kaolin clay or ground calcium carbonate as pigment. They were investigated in a strain rate ranging from 10^3 to 1.25×10^4 s^{-1}. All suspensions exhibited strain thinning and strain hardening at low and high strain rates, respectively. For the kaolin coating colors, a more pronounced dilatancy has been observed. The ratio of extensional to shear viscosity (Trouton ratio) of the suspensions investigated was shown to exceed considerably the theoretical value of three expected for Newtonian fluids. Coating colors showed a Trouton ratio ranging 10 to 20 in the investigated range. Because suspensions made-down with no spherical particles tend to form clusters at high strain rates, a more pronounced effect in both the shear thickening and strain thickening regions was observed with coating colors with delaminated kaolin clay.

Thursday 8:55 Grand Station IV ER3

Elongational Viscosity of narrow molar mass distribution polystyrene

Anders Bach[1], Kristoffer Almdal[2], Henrik K. Rasmussen[3], Kell Mortensen[2], and Ole Hassager[1]
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Transient and steady elongational viscosity has been measured for two narrow molar mass distribution polystyrene melts of molar masses 200,000 and 390,000 by means of a filament stretching rheometer. Total Hencky strains of about 5 have been obtained. The transient elongational viscosity rises above the linear viscoelastic prediction at intermediate strains indicating strain hardening. The steady elongational viscosities are monotone decreasing functions of elongation rate. At elongation rates larger than the inverse reptation time, the steady elongational viscosity scales linearly with molar mass at fixed elongation rate.

Thursday 9:20 Grand Station IV ER4

An extensional viscosity for fluid breakup

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When a fluid breaks up, as when droplets form, the most relevant fluid properties are generally surface tension and viscosity if the fluid is Newtonian. For a non-Newtonian fluid, it is not clear what the additional fluid property should be. This work proposes an extensional flow property for these situations, based on a technique for detecting weak elasticity in extension. In this technique a liquid sample is confined between two small disks and then stretched out in a controlled manner until the liquid bridge breaks. The stretch distance at the break point is noted. Tests with a wide variety of Newtonian fluids established the baseline for inelastic liquids. With an elastic liquid, the breaking length is greater because the additional axial stress delays the pinching off. The extra length is accordingly a measure of the fluid's elasticity in extension. Tests with known weakly elastic liquids confirmed that the extra length is related to fluid elasticity. Breaking length measurements of paper coating suspensions were found to correlate with levels of misting in a coating machine (the misting occurs as a result of film splitting). The fluid property related to breaking length appears to be a type of extensional viscosity, namely a high-strain extensional viscosity. Breaking length measurements were obtained for very dilute solutions of rigid and flexible polymers, and the corresponding values of high-strain extensional viscosity are found to depend linearly on polymer concentration.

Thursday 10:10 Grand Station IV ER5

Fingerprinting polymer macrostructure using the new SER extensional rheometer fixture

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The extensional melt rheology of a series of polymers of varying macrostructure was characterized with the use of the new commercially available SER extensional rheometer fixture. The miniature SER unit has been specifically designed for use as a fixture on a variety of commercially available rotational rheometers and can be accommodated within the smallest of environmental chambers. The extensional melt data indicate that even subtle differences in polymer macrostructure are easily distinguishable with this robust instrument.

Thursday 10:35 Grand Station IV ER6

Prediction of elongational viscosities of polymer melts by stochastic simulation

Jun-ichi Takimoto and Masao Doi
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The elongational viscosities of polydisperse polymer samples are studied by stochastic simulations based on a slip-link model. In this model, it is assumed that exactly two chains are involved in each entanglement. The effects of the reptation, contour length fluctuation and constraint renewal are taken into account in a simple and natural way.

In the case of linear monodisperse polymers, the elongational viscosity shows the strain hardening only if the strain rate is faster than the Rouse relaxation rate. In the case of bidisperse samples, the strain hardening appears when the strain rate is faster than the Rouse relaxation rate of the longer component. Especially, a small amount of very long

chain strongly enhances the strain hardening. This enhancement is not due to the entanglement among long chains; instead, even an isolated long chain can contribute to the strain hardening.

By using the molecular weight distribution of a polydisperse linear polymer sample, our simulation can correctly reproduce the experimentally observed elongational viscosity of the sample. Moreover, effect of adding a small amount of very high molecular weight component to the sample is also well reproduced.

Our simulation method can also be applied to star polymers. Although the linear viscoelastic properties of star polymers are entirely different from those of liner polymers, the nonlinear properties such as the non-Newtonian (steady) shear viscosity, the shear damping function, and the strain hardening of the elongational viscosity are quite similar. For example, the elongational viscosity of a monodisperse star polymer is very close to that of the linear polymer with the same span molecular weight, i.e., with the same Rouse relaxation time. Extension of our method to more general branched polymers will also be discussed. (Our simulation program, PASTA, can be downloaded from http://octa.jp)

Thursday 11:00 Grand Station IV ER7

Recovery and rupture in elongational flow of entangled polymers

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The scaling theory for melt rupture in extensional flow [Joshi and Denn, J. Rheol. 47, 291-298 (2003)] describes the continuum failure of entangled polymers in the regime where the strain is fully recoverable. We describe a methodology to predict rupture in the regime where the extensional flow is dissipative. The scaling theory is used to predict the recoverable portion of the strain at failure, and the total strain and time to rupture are then computed from an appropriate integral constitutive equation. Available integral theories differ considerably in their ability to predict recovery and time to rupture.

Thursday 11:25 Grand Station IV ER8

Relating molecular structure and rheology of model branched polystyrene melts by MSF theory

Manfred H. Wagner[1], Jens Hepperle[2], and Helmut Münstedt[2]
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Recently, Hepperle and Münstedt (2003) reported non-linear elongational and shear measurements on a series of graft-polystyrenes with varying average number and molar mass of grafted side chains. To investigate the relation between branching topology and rheological properties, the experimental data are compared to predictions of the Molecular Stress Function (MSF) model [Wagner et al. (2003)]. This is based on a specific strain energy function, which assumes that the backbone of the grafted molecule is stretched by deformation, while the side chains are compressed. It is demonstrated that the experimentally observed slope of the elongational viscosity after inception of strain-hardening depends on the ratio of total molar mass to backbone molar mass as predicted by the model.

The steady-state (plateau) value of the elongational viscosity depends on the maximum relative stretch, which can be supported by chain segments. It is found that this maximum stretch increases with the molar mass fraction of side chains, and at the same molar mass fraction, more short side chains lead to higher values of the maximum stretch than a few long side chains. Surprisingly, even side chains which are shorter than the entanglement length of linear PS are found to contribute to strain-hardening.

Using the same non-linear parameters as in elongational flow plus a parameter taking into account the additional constraint release in rotational flows, the shear damping function data of the grafted polystyrene melts are modeled quantitatively by the MSF theory.

References:
Hepperle, J., and H. Münstedt (2003), submitted to Macromolecules
Wagner, M.H., M. Yamaguchi, and M. Takahashi, J. Rheol. 47(3) (2003) 779-793

Thursday 11:50 Grand Station IV ER9

Investigation of semihyperbolically converging dies for the measurement of elongational viscosity of polymeric fluids

Kathleen Feigl[1], Brian J. Edwards[2], Franz X. Tanner[1], and John R. Collier[2]
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A method for measuring the elongational viscosity of polymer melts and solutions in die entrance flows is evaluated by means of numerical simulations and experiments. The method involves passing a material through a cylindrical, converging die whose semihyperbolic shape mandates a shear-free, or nearly shear-free, flow within the die, assuming wall slip. An expression for elongational viscosity is derived under less restrictive conditions than in previous studies. This expression consists of two terms, one of which is a measurable effective elongational viscosity defined in terms of the change in pressure over the die, the volumetric flow rate and the Hencky strain determined by the geometry.

To evaluate this method, finite element techniques are used to calculate the flow of a low-density polyethylene melt in two semihyperbolically converging dies. After confirming that purely elongational flow is produced within the die, assuming wall slip, the effective elongational viscosity is computed from the calculated flow field and these values are compared with the values of elongational viscosity found by integrating the constitutive equation for the material in elongational flow. Over the wide range of strain rates considered, very good agreement is found between these two sets of values when the time associated with the effective viscosity is appropriately specified. A similar analysis for a Newtonian fluid shows that the effective elongational viscosity satisfies the Trouton ratio over the range of strain rates considered. These results indicate that the measured effective elongational viscosity is an excellent approximation to the material's true elongational viscosity.

Furthermore, experimental data taken from polymer melts in the semihyperbolically converging die is presented. This data, along with the computer simulations, indicate that semihyperbolically converging dies can be used effectively to obtain transient elongational viscosity measurements at constant strain or constant strain rate.

Symposium LC
Liquid Crystalline Polymers and Self-Assembling Fluids

Organizers: Karen Winey and Peter Olmsted

Thursday 8:05 Grand Station V LC19

Solution rheology of comb-like associative polymers: Effects of backbone composition and hydrophobe concentration

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We investigate the effects of polymer molecular structure on the solution rheology of a hydrophobically modified associative polymer comprised of macromonomers with alkyl hydrophobes attached to a poly(ethyl acrylate-co-methacrylic acid) backbone. In particular, the effect of polymer backbone composition with variable proportions of methacrylic acid (MAA) and ethyl acrylate (EA) are examined. We find that the concentration of the MAA monomer has a large impact on polymer viscoelasticity. Polymers with low MAA content have smaller hydrodynamic size that result in lower viscosities and dynamic elastic moduli compared to polymers with high MAA content. Moreover, the balance between the polymer hydrodynamic size, the chain flexibility, and the aggregation of the EA blocks yield maxima in these material functions with respect to the MAA concentration. The scaling of shear viscosity, high frequency elastic modulus, and creep compliance with polymer concentration exhibits power-law behavior with different exponents. In all cases, three power-law regimes are observed, regardless of the MAA content. However, the transitions shift to lower concentrations as the MAA content increases. The scaling behavior in the three regions can be attributed to the presence of different hydrophobic interaction modes and are compared to theoretical predictions based on the sticky Rouse and sticky reptation models. We observe a substantial increase in viscosity at intermediate macromonomer content (1 mole%), possibly due to an increase in the number of intermolecular junctions as the number of hydrophobes per chain increases. This is in contrast to (i) low macromonomer concentration (0.3 mole%) behavior that reveals low viscosity due to weak hydrophobic associations, and, (ii) high macromonomer concentration (1.9 mole%) behavior that favors more intramolecular association resulting in lower viscoelastic properties compared to intermediate macromonomer concentrations.

Thursday 8:30 Grand Station V LC20

Reverse gelation of associative network polymers

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Soft solids get easily broken (internally and/or macroscopically) at loads above their yield stress. While chemical network polymers break irreversibly, associative networks are able to heal their structure into long-range connectivity, often of increased order. The dynamics of formation, breaking, and reformation of soft polymer gels can be observed with rheology. Typically, the controlling parameters are stress, strain, temperature, and time. Here we are concerned with S-EB-S (polystyrene- polyethylene/ buthylene-polystyrene) triblock copolymers of which the midblock is selectively swollen with an oil. Below their order-disorder-transition temperature (ODT), such polymer /solvent systems are able to nano-phase separate into spherical polystyrene domains (5-50 nm scale) in a continuous matrix of EB swollen by solvent, hereby ordering into a body centered cubic lattice. The kinetics and dynamics of reverse gelation (breaking) and gelation will be discussed in relation to the S-EB-S model polymer.

Thursday 8:55 Grand Station V LC21

Characteristic rheological behaviour of associating polymers

Linda Pellens, Rogelio Gamez Corrales, Jan Vermant, and Jan Mewis
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It has been investigated whether common features can be identified that characteristize associative behaviour, irrespective of the polymer being telechelic or not. For the steady state viscosity curves, the Cox-Merz analogy does not hold for these materials. A modified Cox-Merz rule that applies to the normal stresses of common polymers also fails in the case of associative polymers. Although the viscosity curves can have different shapes, a general pattern can be detected in the strain dependence of the dynamic moduli and in the nonlinear relaxation functions. The latter indicate that strain hardening is associated with short time phenomena, whereas the strain softening that appears at larger strains starts at longer times. Parallel superposition measurements have been used to explore the frequency dependence of the mechanisms that contribute to the steady state shear properties. At high frequencies a characteristic increase in both superposition moduli appears, even for the shear thinning solutions. This also seems to be characteristic for associating polymers. The time and frequency dependence of these features can be used to assess the underlying molecular mechanisms.

Thursday 9:20 Grand Station V LC22

Structure-rheology relationships for associative polymers based on polyoxyethylene macromers: A polysoap treatment

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Water soluble polymers with covalently bound non-ionic polyoxyethylene-based amphiphiles may be considered as 'polysoaps'. In the dilute concentration regime, the bound amphiphiles separated by hydrophilic strands of polymer backbone self-assemble in an intramolecular fashion. The hydrophobes of the bound amphiphiles cluster to form a micellar core surrounded by a hydrophilic 'corona' comprising the polyoxyethylene spacer groups and looped strands of polymer backbone. Micellization is favored by the creation of the core-water interface and by the transfer of the hydrophobes from the water phase into the core. However, this process is opposed by coronal loop repulsion, which results in a substantial free energy penalty. At higher concentrations, such materials find practical use as rheology modifiers. Thus, above the threshold where a sample spanning transient network is formed, interchain bridging interactions control the connectivity or mechanical interaction density. The intermolecular association is dictated by the balance between osmotic repulsion between the coronal loops and the 'bridging attraction' resulting from the exchange of amphiphiles. We present data from rheometry and dynamic light scattering experiments and demonstrate that the polysoap model may be useful in interpreting structure-rheology relationships in industrially important rheology modifies such as acrylic HASE polymers.

Thursday 10:10 Grand Station V LC23

Amphiphilic block copolypeptide hydrogels: Tuning gel rheology through molecular architecture

Victor Breedveld[1], Andrew Nowak[2], Timothy J. Deming[3], and David J. Pine[4]

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Recent developments have enabled the synthesis of amphiphilic block copolypeptides of well-controlled length and block composition. In addition to their biochemical functionality, the polypeptide blocks can exhibit secondary structure (α-helix or β-sheet) as opposed to conventional block copolymers with random coil configuration. The molecular conformation gives rise to new mechanisms of self-assembly that control the properties of block copolypeptides in solution.

We will present rheological data on aqueous solutions of diblock amphiphiles consisting of a water soluble polyelectrolyte block (lysine, glutamic acid) and a hydrophobic block of varying composition. These block copolymers self-assemble due to their amphiphilic nature and at remarkably low concentrations (as low as 0.25% by weight) they can form strong, porous hydrogels. The gelation concentration is a strong function of molecular weight, relative block length and secondary block structure.

The mechanism of gelation was investigated by systematically tuning molecular parameters (molecular weight, relative block lengths, secondary structure, amino acids) and solvent properties (salt concentration and pH). The delicate balance between repulsive and attractive intermolecular forces could be manipulated so that the addition of salt strengthens the hydrogel. Rheological data in combination with direct imaging techniques (confocal and electron microscopy) helped to optimize the design of these unique block copolypeptide hydrogels for potential applications in tissue scaffolding and drug delivery.

Thursday 10:35 Grand Station V LC24

Strong gels from associative PLA-PEO-PLA triblock copolymers

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Soft biomaterials derived from amphiphilic polymers have received considerable attention in the last decade. In particular, hydrogels based on copolymers of poly(lactic acid) (PLA) and poly(ethylene oxide) have been studied extensively due to their biocompatibility and biodegradation characteristics. However, the rheological properties of these systems have remained largely unexplored; moreover, control of the rheology to mimic that of surrounding tissue is crucial to in vivo applications. We present experimental results of the viscoelastic moduli for aqueous gels of PLA-PEO-PLA triblock copolymers. These copolymers are analogous to telechelic hydrophobically-modified PEO systems and self-assemble to form associative networks in aqueous media. The elastic moduli of our PLA-PEO-PLA gels are orders of magnitude higher than those observed for other aqueous physically-associated gels. In addition, the value of G' is extremely sensitive to the length of the PLA hydrophobe, giving us a molecular knob that we can use to tune the rheology for specific applications. We have also explored the effect of crystallinity of the hydrophobic domains on the rheology by utilizing triblocks with varying degrees of D- and L- lactide. This allows us to go from network junction points with a high degree of crystallinty (triblocks with PLLA hydrophobes) to those that are amorphous (triblocks with PDLLA hydrophobes). Finally, we have examined the rheological behavior of these solutions as a function of temperature. Many systems exhibit a decrease in the viscoelastic moduli with increasing temperature and undergo a gel-liquid transition with $G' \sim G''$ at a critical temperature. However, some systems display non-monotonic behavior and show an increase in G' at higher temperatures. We believe this effect may be due to dehydration of the PEO groups at high temperatures, and that it could offer the possibility of designing a triblock with a liquid-gel transition near physiological temperatures.

Thursday 11:00 Grand Station V LC25

Linear viscoelasticity of telechelic fluoroalkyl PEGs

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Centre for Water Soluble Polymers, North East Wales Institute, Wrexham LL11 2AW, United Kingdom

The aqueous solution rheology of hydrophobically associating polymers based on poly(ethylene glycol) end-capped with partially fluorinated alkyl groups is reported. The current model concerning the network topology of such polymers relies upon the self-assembly of the hydrophobic end-groups to give flower-type micelles in the dilute concentration regime and a 3-D transient network at high polymer concentrations through intermolecular association. Micelles composed of approximately 10 polymer chains are estimated through dynamic light scattering studies at concentrations above the onset of association. The results of the present study indicate that the linear viscoelasticity is characterised by a number of unusual features, not previously observed for telechelic hydrocarbon end-capped poly(ethylene glycol). Firstly, the frequency dependence of the small deformation moduli deviates strongly from the simple Maxwellian response usually observed for polymers of this type. Specifically a low frequency plateau in the storage modulus is observed, together with evidence of an additional fast relaxation process at short timescales. In addition the concentration dependence of the zero shear viscosity is characterised by several regimes, described by different scaling exponents. Importantly, our findings appear in good agreement with the recent theoretical treatments of comb-type associative polymers bearing many hydrophobic sticker groups [Rubinstein and Semenov (2001)]. We link the concentration corresponding to the onset of a large increase in zero shear viscosity to the formation of an infinite percolation network comprised of long strings of super-bridged micelles which is not space filling. A revised model for the network topology of telechelic associative polymers is presented as a result of our findings.

Thursday 11:25 Grand Station V LC26

On the weak nematic elasticity

Arkady I. Leonov[1] and Valerii S. Volkov[2]
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The paper investigates the general case of incompressible non-classical elasticity with small deformations and rotations. It is shown that the internal spin rotations are important only when a specific Born term is presented in the free energy. The thermodynamic stability conditions and existence of soft deformational modes are analysed for free energy with three rotational degrees of freedom and scalar order parameter. It is shown that the soft deformation modes do not always exist. If the conditions for existence of soft modes are satisfied and the Born term is absent, the stress tensor is proved to be symmetric. It is shown that the infinitesimal Warner potential satisfies these conditions. When the stress symmetry could be assumed only approximately, a simplified "reduced" relations are derived for the free energy and stress. The reduce formulation, which preserves the general stability conditions and the condition for existence of soft deformations, also allows easy calculations of stress-strain-rotation relations.

Thursday 11:50 Grand Station V LC27

Anomalous rheology in a diblock copolymer/hydrocarbon system and its kinetic origin

Zhizhong Liu and Montgomery T. Shaw
Chemical Engineering, University of Connecticut, Storrs, CT 06269

Squalane solutions (5 to 20 wt.%) of a diblock copolymer, poly(styrene-b- hydrogenated isoprene) (SEP, Kraton G1702), were prepared by a cosolvent-casting method. The as-cast solutions behaved as viscous liquids with terminal flow behavior at room temperature. Upon heating, the storage modulus increased abruptly and rose by a factor of more than 3 within a temperature range of 30 °C. It exceeded the loss modulus at about 35 °C and 70 °C for the 5 % and 10 wt % solutions, respectively. At high temperatures, dynamic frequency sweeps demonstrated that the solutions had gelled. The solutions did not recover to their starting liquid-like behavior on cooling. SAXS revealed a random array of spherical micelles in the as-cast solutions at room temperature, which is hypothesized to be a nonequilibrium state that was formed by dynamic arrest during solution preparation. The abnormal solidification with increasing temperature was correlated with the formation of body-centered cubic (BCC) structures in the solutions. Isothermal SAXS measurements also indicated that the rate of formation of BCC structures in the as-cast SEP/squalane solutions increases with temperature and decreases with polymer

concentration. A diffusion-controlled nucleation and growth mechanism was proposed for the ordering process in SEP/squalane solutions at temperatures far below the order-disorder transition temperature (ODT).

Poster Session

Symposium PO

Organizer: Surita Bhatia

Wednesday 6:00 Reflections/Waterfront PO1

Microhydrodynamics of concentrated hard sphere suspensions by particle-tracking confocal microscopy

Qiang Lu, Clare Dibble, and Michael Solomon
Chemical Engineering, University of Michigan, Ann Arbor, MI

The passive, correlated Brownian motion of concentrated suspensions of hard sphere colloids is studied as a function of the separation distance between particles. Such particle dynamics are of fundamental interest because they quantify the strength and range of hydrodynamic interactions at volume fractions for which many-body effects are important. The results may be applied to better understand suspension hydrodynamics in the volume fraction range at which the colloidal glass transition occurs and for which simulation methods, such as Stokesian dynamics, become increasingly expensive. We have synthesized fluorescent poly(methyl methacrylate) colloids which have been reported to crystallize at volume fractions consistent with the hard sphere interaction potential [Campbell and Bartlett, Journal of Colloid and Interface Science, 256 325 (2002)]. The Brownian motion of all colloids within a two-dimensional plane deep within high volume fraction samples has been monitored by time-resolved confocal laser scanning microscopy. By means of quantitative image analysis, we measure the effect of volume fraction on the single-particle mean square displacement, the distribution of single-particle displacements, and the cross-correlation of the displacement of particle pairs separated by a distance, r. The results are discussed in light of recent simulations, scattering studies and direct visualizations of particle motions in colloidal suspensions.

Wednesday 6:00 Reflections/Waterfront PO2

Dynamics and structure of dense colloid polymer mixtures

Subramanian Ramakrishnan, Yeng-Long Chen, Syed Shah, Kenneth Schweizer, and Charles Zukoski
Chemical and Biomolecular Engineering, Universiy of Illinois, Urbana, IL 61801

Tuning interactions between colloidal particles such that they assemble into useful structures is an important step in the success of many technologically significant applications. The advantage of working with colloid-polymer mixtures is the ability to fine tune the microstructure and hence the flow properties with two independent variables : the concentration of added polymer (c_p) and the size of the polymer (R_g). In this work we report on ultra small angle X-ray scattering measurements of structure of a model colloid-polymer system over a wide range of experimental conditions. Special emphasis is given to the conditions under which the colloidal particles undergo a non-equilibrium gel transition. The structure factor of the system is measured deep inside the gel region at a constant polymer concentration for varying colloid volume fraction. Rheological measurements of the elastic modulus and the shear viscosity are then made under identical conditions in attempt to correlate structure with rheology. Comparisons are then made with mode coupling theory with accurate, no adjustable parameter models of input to predict the gelation boundaries and elastic shear moduli. Different scalings for the moduli and yield stress based on the fractal nature of the aggregated suspensions are also tested.

Wednesday 6:00 Reflections/Waterfront PO3

Shear and extensional thickening of filled silica suspensions

Giorgia Bettin and Gareth H. McKinley

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

The rheological response of high concentration silica suspensions in shearing and extensional deformations is presented. The behavior of these shear-thickening fluids is of particular interest for possible applications in energy shunting and load dissipation, as well as in biomedical applications. Two different types of silica particles are studied: the first are polydisperse and non spherical, with a median diameter of 1.7 ìm and standard deviation of 1.4 ìm, secondly we also examine fluids composed of monodisperse spherical particles of 0.3 or 1 ìm diameter (standard deviation of 0.03 and 0.1 ìm respectively). The particles are dispersed in ethylene glycol at volume fractions of up to 47% for the polydisperse sample and up to 60% for the monodisperse spheres. The behavior of the silica suspensions is studied under steady shear, small and large amplitude oscillatory shear flow and also in transient extensional flow. Particular attention is given to the effect of slip and a number of roughened surfaces are utilized to minimize its effects. Results show that in the shearing deformations, extreme shear thickening occurs at higher volume fraction for the monodisperse spherical particles, (ca. 57%) , while the polydisperse suspensions exhibit shear thickening at much lower volume fraction (45%); presumably due to the irregular shape of the polydisperse particles. Oscillatory experiments over a wide range of imposed oscillatory deformations indicate that both the onset and magnitude of the shear thickening depend on the frequency and strain applied. These results can be represented on a Pipkin diagram and show that rapid time-varying deformations result in maximum energy dissipation). Two different regimes are found through extensional flow measurement: at low extension rates the suspensions respond as a viscous rate-thinning fluid, whereas beyond a critical extension rate, the suspension strain-hardens and ultimately fractures in a solid-like fashion.

Wednesday 6:00 Reflections/Waterfront PO4

Direct imaging of three-dimensional structure of colloidal gels by confocal microscopy

Myung Han Lee and Eric M. Furst

Chemical Engineering Department, University of Delaware, Newark, DE 19711

Core-shell silica particles, with the diameter of 1.5 ìm, containing a dye fluorescein isothiocyanate (FITC), were synthesized by the hydrolysis and condensation of tetraethylorthosilicate (TEOS). Sodium dodecyl sulfate (SDS) was added to synthesize fluorescent core particles with the size of 1.0 ìm. The silica particles with a fluorescent core and a non-fluorescent shell were sterically stabilized by chemisorption of octadecanol at the surface. Octadecyl coated silica particles were dispersed in organic solvents, chloroform and hexadecane, with refractive index close to that of silica. In chloroform the low dielectric constant of solvent and hydrophobic property of the modified particle result in stabilizing silica particles. However, silica particles dispersed in hexadecane formed a gel at room temperature. Finally, 3D images of colloidal gels were obtained by locating the particle positions. The microstructure of the gel was characterized while varying the volume fraction of particles.

Wednesday 6:00 Reflections/Waterfront PO5

Real-time X-ray radiography of a bubble rising through a concentrated suspension

Anne M. Grillet[1], Lisa A. Mondy[1], Vibha Chawla[2], and Alan Graham[2]

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[2]Chemical Engineering Department, Texas Tech University, Lubbock, TX

Micro-focus X-ray inspection has long been used as a method to detect defects such as cracks or voids inside solid parts. Because the unique capability to image inside optically opaque systems, real-time micro-focus X-ray imaging has recently been applied to study the dynamics of bubbles rising inside suspensions. We have performed our experiments using a Syburg micro-focus X-ray with a 2 micron spot size using a projection imaging method. X-rays are passed through the fluid container and are collected on an image intensifier that converts the attenuated X-rays to visible light. X-rays that have passed through the bubble are not attenuated as much as X-rays which pass only through the suspension, resulting in a bright spot on the visual image. By analyzing the image, the size and velocity of the bubble can be tracked as it travels through the fluid. We present our initial efforts to validate X-ray imaging as a quantitative tool to measure the size and velocity of a rising gas bubble in a quiescent clear fluid using simultaneous video imaging. We then present measurements taken in clear and opaque suspensions with both traditional video imaging as well as X-ray radiography.

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 6:00 Reflections/Waterfront PO6

Microrheology of dense colloidal suspensions

Alexander Meyer, Myung Han Lee, and Eric M. Furst
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We will present novel methods of performing microrheology in dense colloidal suspensions using direct manipulation of probe particles with laser tweezers. A silica suspension refractive index-matched in hexdecane is seeded with index mismatched particles. Simultaneous measurements of the suspension microstructure are made using fluorescence confocal microscopy. From the response of the probe particle, we calculate local rheological and mechanical properties of the suspension and correlate them with the microstructure. This enables us to directly relate rheological properties to microstructural rearrangements.

Wednesday 6:00 Reflections/Waterfront PO7

Effect of particle surface modification in concentrated suspension on rheological behavior

Akio Hamamoto[1] and Susan J. Muller[2]
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The effect of particle surface modification on the rheological behavior of several concentrated suspensions is investigated. The experiments we present are carried out using spherical silica particles coated with polydimethylsiloxane, methylhydrogen polysiloxane and n-octyl triethoxy silane as the treatment agents. These types of surface treatment have been adopted in the cosmetics field and were supplied by Daito Kasei Kogyo Co. (Osaka, Japan). . The coated particles are dispersed in tetradecane and polydimethylsiloxanes of varying viscosity as the solvent. In addition, suspensions of the un-coated particles are prepared using aqueous solvents of different pH. The viscosity of the concentrated suspensions of the bare particles depends on the pH value and the volume fraction of the solution. Lower pH or higher concentration of particles produces higher suspension viscosities. In addition, this type of highly concentrated suspension shows shear thickening at high shear rates, and increasing pH results in a higher critical shear rate for the onset of shear thickening. Moreover, in the case of surface modified particle suspensions, the viscosity depends significantly on the type of surface treatment. Although the molecular weights and chemical structures of the polydimethylsiloxane and methylhydrogen polysiloxane agents are similar, the magnitude of the viscosity at comparable volume fraction differs dramatically. In this presentation we will discuss the relationship between each particle surface modification and the suspension viscosity.

Wednesday 6:00 Reflections/Waterfront PO8

Experimental observation of the pair-distribution function in concentrated suspensions

Jing Fan[1], Alan Graham[1], James Abbott[1], and Lorne A. Davis[2]
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A rich variety of Non-Newtonian behaviors such as normal stresses and shear thinning at high solid loading have been observed even in the simplest model systems such as suspensions of neutrally-buoyant spheres in Newtonian liquids. There is a growing body of experimental, numerical and theoretical work that links the origin of non-Newtonian behaviors to flow-induced asymmetries in the pair-distribution function for particles in suspensions. However, little work has been done based on direct experimental observation 3D particle locations in suspensions.

It is now possible with NMR and X-ray tomography to determine the microstructure of large volumes with micron level resolution. In this work, two suspensions of monodisperse sphere at volume concentrations of 50% were prepared and subjected to flows in two wide-gap Couette cylinders. The particles in the two suspensions were 1/8Ó and 1/16Ó PMMA spheres respectively. The evolution of 3D configuration of particles in two initially well-mixed suspensions under shear flow was measured by both NMR and X-ray imaging systems. The data reduction method accounted for finite containers with curved boundaries and was validated using simulated equilibrium particle configurations. The comparison between the results of simulation and experiment showed that the uncertainties of particle center dramatically reduced the value of the first peak of pair distribution function. No significant asymmetries in the PDF were observed after shearing when results were projected onto the shear plane.

Wednesday 6:00 Reflections/Waterfront PO9

Shear-thinning of polydisperse suspensions

Alan Graham, James Abbott, Vibha Chawla, Rahul S. Admuthe, and Patrick Reardon
Chemical Engineering Department, Texas Tech University, Lubbock, TX

The effects of the polydispersivity of the particle phase on the rheology of suspensions are studied with falling-ball rheometry. The model suspensions consist of large, neutrally buoyant spheres in a viscous Newtonian suspending fluid. The experiments determine the average velocity of the settling particle along the centerline or axis of the containing cylinders. Here the relative viscosity, η_r, is defined as the resistance of a falling ball relative to that experienced in the pure suspending fluid. The experiments are performed in cylinders far enough from the upper and lower surfaces to avoid end effects. The objective of this study was to determine the effects of the dispersivity of the particulate phase on the relative viscosity of the suspensions. In dilute and moderately concentrated suspensions (volume fraction of solids, $\phi\eta_r$ between the model suspensions of spheres of uniform sizes and suspensions of spheres with polydisperse sizes for all settling sphere sizes examined. These observations are in agreement with Einstein's theory for infinitely dilute suspensions that predicts the viscosity is independent of the size and distribution of suspended particles. As ϕ increases to 0.5, suspensions made up of particles with very narrow size distributions have viscosities that are essentially shear-rate independent. As the standard deviation of the particle distribution normalized by the average particle size increases from 0.01 to 0.2, we find that η_r exhibits significant shear thinning with a power law exponent, n, decreasing to 0.50 from the roughly Newtonian behavior (n=1). Over the range of our data, η_r increased as the degree of polydispersivity increased.

Wednesday 6:00 Reflections/Waterfront PO10

Stress fluctuations of a jammed emulsion under shear

Gladys Massiera and John C. Crocker
Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA

We use a concentrated emulsion as a model system, to study dynamical length scales involved in a material near the jamming transition. The emulsion is index and density matched. Colloids are incorporated in the emulsion as probes. We use a custom-built apparatus to measure the beads mean square displacement under steady shear. The emulsion is sheared in a rectangular capillary, and observed simultaneously under an inverted microscope. Beads are agitated by rearrangements of the oil droplets, and the one and two point mean-squared displacements are measured. By combining this data with macroscopic rheology, we can gain insight into the stress fluctuations when shear is applied. Such an experiment may be useful to test concepts of effective temperatures suggested by simulations for other non-thermal systems such as foams or granular systems.

Wednesday 6:00 Reflections/Waterfront PO11

Flow properties of thermo-responsive Fluids

Prashant Mullick and Charles F. Zukoski
Department of Chemical and Biomolecular Engineering, University of Illinois, Urbana, IL 61820

Responsive fluids are soft materials that change microstructure and/or mechanical properties upon small changes of an external driving force. The driving force can be in the form of changes in the temperature, pH or ionic strength of the solution. Such fluids have potential applications in bio-separations, drug delivery, smart sensors and actuators and a variety of applications where a rapid and reversible response is desired from the system. The mechanism we have chosen as the basis for developing responsive fluids is the use depletion forces to modulate interparticle interactions. In this work we report on the flow properties and ultra-small angle x-ray scattering (USAXS) measurements for a mixture of hard silica particles and crosslinked poly(N-isopropylacrylamide) microgel soft particles. The thermoresponsive nature of the poly(N-isopropylacrylamide) microgel particles has been well studied. These microgel particles show drastic changes in the size of single particles over a small range of temperature. We use this effect to control the interaction potential of the larger silica spheres. The phase diagram of the mixture of these particles shows that the formation of gel phases occurs in a region that is neither predicted by simple depletion models nor models described by simple mixture of hard spheres. The structure factor of the mixture is measured by USAXS deep into the gel phase and shows distinct clustering of the silica particles and the structure is unaffected by further addition of microgel particles beyond the formation of the gel phase. Stress viscometry and low amplitude oscillatory measurements as a function of increasing microgel concentrations up to and beyond the gel boundary are performed.

Wednesday 6:00 Reflections/Waterfront PO12

Shear effects on microstructural dynamics of biopolymer microemulsions

Jerry Nesamony and William M. Kolling

School of Pharmacy, The University of Louisiana at Monroe, Monroe, LA 71209

Water domains within water-in-oil (w/o) microemulsions can exist in a variety of structures and these systems may possess interesting rheological properties owing to differences in interfacial area of the various ordered structures. The purpose of this work was to study the effect of shear on microstructural dynamics of w/o microemulsions of aqueous sodium alginate/Aerosol OT (AOT)/isopropyl myristate (IPM) systems in order to develop correlations between formulation parameters and flow properties. Microemulsions were prepared by adding various amounts of water or aqueous sodium alginate of three different concentrations (0.1, 0.2, and 0.4% w/v) to a 1 M solution of AOT in IPM to produce systems of varying Wo's (Wo = [water]/[surfactant]). Shear rates in the range 0 to 5000 1/s were applied for different durations using a controlled stress rheometer. The rheological properties of water/AOT/IPM microemulsions showed moderate deviations from Newtonian behavior as demonstrated by the rate indices. The viscosity of both water and alginate microemulsions paralleled increases in Wo. Microemulsions prepared using 0.2% alginate solutions demonstrated the maximum increase in viscosity of 27% at Wo = 20 when compared to Wo = 5. When shear was applied for greater durations of time, a Wo dependant shear thinning effect was observed in all microemulsions. The effect was significant at Wo = 10, 15, and 20 for 0.1% alginate/AOT/IPM systems but was seen at all Wo values for 0.2% and 0.4%. Fluctuations in normal force values were observed at low shear rates, and a slight increase in the same values was seen at higher shear. The changes in the delineated flow properties indicate rich microstructural dynamics in the microemulsions. The effect of shear on the normal force values suggests transitions in the organized structure of the aqueous domain. These microemulsions could find use as templates for enzyme immobilization, nanoparticle synthesis, or as endocytotic carriers for DNA or polypeptides.

Wednesday 6:00 Reflections/Waterfront PO13

Red blood cell deformation under shear and elongational flow

Sung Sik Lee, Nahn Ju Kim, Sang Kook Lee, Kyung Hyun Ahn, and Seung Jong Lee

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Understanding the response of Red Blood Cell (RBC) to the mechanical stress in shear and extensional flow is meaningful in both clinical and rheological point of view. Rheologically, RBC is deformable capsule dispersed in the complex medium, plasma. Also clinically, shear-induced damage of RBC is a major problem in the practical use of artificial organs in extra corporeal circulation. For designing and operating artificial organs in a safe mode, many researchers have tried to correlate the amount of shear stress and the mechanical damage. In this study, we investigated RBC deformation and damage by controlling the shear and elongation flow in the flow cells and PDMS-glass hybrid micro channels. RBC suspended in poly(vinyl) pirrolidone (PVP) solution was inputted into the flow cells and microchannels, and the images were captured during the flow. The degree of deformation and damage were measured and analyzed with the captured images. Also, computer simulation was carried out using CFD package (CFD-ACE+), and the results were compared with the images to figure out the characteristics of flow field in the microchannel. In the flow cells, the RBC orients along the flow direction when it experiences shear, and it changes its shape gradually from the biconcave towards a prolate as the shear stress is increased. And in the cross microchannels, the degree of deformation changes according to the position in the channel or to the flow field which consists of shear and elongation flow. We have shown that the elongational flow in the cross micro-channel induces significant cell deformation, and that the elongational flow could be one of the dominant factors for RBC deformation.

Wednesday 6:00 Reflections/Waterfront PO14

Effect of drag-reducing polymers on red blood cells in microchannel flow

Zhongjun J. Wu[1], Philip J. Marascalco[2], Garrett C. Smith[2], Joie N. Marhefka[2], and Marina V. Kameneva[1]
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It has been shown previously that minute concentrations of soluble drag-reducing polymers (DRPs) injected in blood of experimental animals significantly increases tissue perfusion and oxygenation. To date, the mechanisms regarding these intravascular effects of DRPs remain unclear. In an attempt to elucidate a mechanism, we examined the effect of DRPs on the in vitro flow behavior of red blood cells (RBCs) in microchannels.

Polyethylene oxide WSR-301 (PEO-WSR) and polyethylene oxide with molecular weights of 200 kD (PEO-200) were used in the study. WSR is a well-known DRP and PEO-200 has no drag-reducing ability. Each polymer was added at concentrations of 0, 5 and 10 ppm to suspensions of rat RBCs at 20% hematocrit and pumped with a syringe pump through a 100×100×2500 micron channel at several flow rates. The discrete deforming and moving RBCs under shear flow were visualized via an inverted microscope with stroboscopic lighting.

The addition of the PEO-WSR significantly increased the RBC deformation and reduced the near-wall cell-free plasma layer. However, no changes in RBC deformation were observed in solutions of PEO-200 and with no polymer added. This suggests that the drag-reducing ability of PEO-WSR is the primary factor in the phenomenon observed in these in vitro experiments.

The decrease in the thickness of the near-wall cell-free layer and increase in deformation of RBCs might increase local hematocrit in microvessels and facilitate oxygen delivery to tissues. These results may offer an explanation for the previously observed increases in microcirculatory blood flow and tissue oxygenation after DRP injection.

Wednesday 6:00 Reflections/Waterfront PO15

The effects of particles on the degradation of drag-reducing polymers (DRP) in flow

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It was discovered several decades ago that the addition of minute amounts of certain soluble DRPs significantly decreases flow resistance without affecting viscosity or density of the fluid in turbulent flow conditions. More recently, blood soluble DRPs have been shown to increase blood flow and tissue oxygenation in animal models. High molecular weight polyethylene oxide (PEO) was shown to be one of the best drag reducers, but it mechanically degrades in turbulent pipe flow and other high shear stress conditions. The degradation is represented by a significant reduction in molecular weight and causes the drag-reducing effect to diminish over a relatively short exposure time. In blood flow, the motion of the red blood cells (RBCs) creates additional flow disturbances and localized turbulence. Here, the degradation of DRPs, including well known DRPs such as PEOs and a novel DRP, a polysaccharide derived from a plant (PDP), was studied under turbulent flow conditions both in saline and in the presence of flowing particles, including RBCs and synthetic particles, at a constant shear stress of 40 N/m^2. PDP was discovered to be much more resistant to mechanical degradation caused by exposure to turbulent flow than PEO in all suspensions. PEO degraded significantly faster in the presence of flowing particles than in saline while the presence of particles only slightly increased the degradation rate of PDP. Under the studied flow conditions, the PEO almost completely lost its drag-reducing ability in one hour in saline and in five minutes in a 20% RBC suspension. The PDP, on the other hand, retained about 50% of its original drag-reducing ability at the completion of the five-hour experiment in saline and about 30% of its original drag-reducing ability after 5 hours in a 20% RBC suspension. Gel permeation chromatography showed a significant decrease in molecular weight (MW) of PEO with increased exposure time in turbulent flow but showed little change in the MW of PDP.

Wednesday 6:00 Reflections/Waterfront PO16

Quantification and characterization of DNA damage induced by the Fenton reaction and pyrogallol using a novel falling needle viscometric assay

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The Fenton Reaction in the human body involves iron (II) and hydrogen peroxide, producing dangerous reactive oxygen species. Iron (II) acts as catalyst and the reactive oxygen species attack DNA, causing DNA strand breaks. A novel viscosity method was introduced to quantify and characterize DNA damage. The Disposable Falling Needle Viscometer (FNV) yields instantaneous readings whereas electrophoresis takes several hours. Unlike electrophoresis, FNV can take measurements of the same sample over unlimited time, allowing for easy characterization of DNA damage behavior. The amount of viscosity dropped directly correlates with the amount of DNA damage occurred. Pyrogallol, a phenol, has been proposed as having antioxidant properties. The prooxidant effects of Pyrogallol in the absence and presence of iron (II) on DNA were studied. Effects of temperature and buffers on DNA were also studied.

As hydrogen peroxide concentration increased (0-100 mM) in the presence of 0.1 mM iron (II), the amount of DNA damage increased. The same trend and greater amounts of DNA damage were observed when iron (II) concentration increased (0-1.5 mM) in the presence of 19.8 and 100 mM hydrogen peroxide. Increasing Pyrogallol concentration (0-1.5 mM) induced DNA damage; however, DNA damage was tripled when 0.1 mM iron (II) was added to Pyrogallol. Electrophoresis tests verified viscometric results, emphasizing FNV as a unique instrument to instantly quantify and characterize DNA damage.

The FNV is an ideal instrument for measuring DNA strand breakage because the FNV provides minimal disturbance of the mechanical structure of DNA with a gentle needle passage, and allows for unlimited measurements. Viscosity measurement is obtained by using the falling time of the needle through the fluid.

Wednesday 6:00 Reflections/Waterfront PO17

DNA molecular configurations in flows near a glass surface

Lin Fang, Lei Li, Hua Hu, and Ronald G. Larson
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In this work, we use λ-phage and T2-coliphage DNA molecules to investigate macromolecular behavior near adsorbing and non-adsorbing glass surfaces under flow. In a steady torsional shear flow and a slit-microchannel flow, we confirm the results obtained in the bulk shear flow by Smith et al. (1999). However, over a region near the surface whose distance from the surface extends up to about 1/3 of the contour length of the DNA molecule, we observe that the number density and average stretch of DNA molecules are lower than in the bulk. In addition, under a steady torsional shear flow, the average stretch $\langle x \rangle$ of λ-phage DNA molecules adsorbed onto the surface is only 3.5 μm at $Wi = 21.5$, which is much smaller than in the bulk. The experimental stretch agrees with Brownian dynamics simulation results in the bulk, but for molecules both near the surface and adsorbed to it, the experimental stretch is much less than that predicted by the simulation (Chopra et al. 2003).

Wednesday 6:00 Reflections/Waterfront PO18

Motions of single protein filaments F-actin in the entangled isotropic networks and in the nematic liquid crystalline phase

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The cytoskeletal protein actin self-assembles to form long and stiff filaments, F-actin, which serves essential functions in cells, such as control of cell shape, division, and motility. In vitro, suspensions of the reconstituted protein filaments F-actin form entangled networks, and as predicted by the Onsager theory, undergo the isotropic-nematic (I-N) liquid crystalline transition at less than 1% wt protein content. Following our recent finding that the I-N transition of F-actin is continuous (Viamontes and Tang, Phys Rev E, 2003), we performed a systematic study of filament motions and alignment traversing the I-N phase transition, using microscopy techniques combining fluorescence imaging, filament tracking, and local birefringence measurements. Among the interesting findings, we detect the Brownian motions of F-actin to be confined within a virtual tube and along the filament axis. The frictional coefficient increases non-monotonically as a function of the protein concentration. A peak value is detected at the onset of strong entanglement, followed by a plateau region of constant diffusion coefficient until the onset of the I-N transition. Surprisingly, the longitudinal diffusion coefficient decreases for filaments in the concentrated nematic state. These findings may be explained based on the tube model for rigid polymer networks.

Wednesday 6:00 Reflections/Waterfront PO19

One and two point microrheology of actin solutions

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We compare one and two point microrheological measurements on entangled F-actin solutions obtained from the thermal fluctuations of pairs of embedded probe spheres held at varying distances in two separate optical tweezers. The position fluctuations were measured with optical interferometry up to frequencies of 195 kHz. The cross-correlated thermal motions of particle pairs at wide separations (two-point microrheology) are related to the bulk viscoelastic properties of the actin solutions. The one-point thermal fluctuations, on the other hand, reflect the local mechanical properties of the solution surrounding the particles. We show that the viscoelastic moduli obtained from one-point microrheology differ significantly from the two-point moduli, which we interpret in terms of the depletion of F-actin from the probe particle surface.

Wednesday 6:00 Reflections/Waterfront PO20

Viscoelastic properties of hydrogels formed via intramolecular folding and self-assembly of amphiphilic β-hairpin molecules

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In this work we studied the viscoelastic properties of the hydrogels formed via intramolecular folding and consequent self-assembly of 20 aminoacid long β-hairpin peptide molecules. These hairpin molecules are amphiphilic in nature with an alternating sequence of hydrophobic valine and hydrophilic lysine amino acids. These molecules are found to form hydrogels with a unique microstructure and nanostructure at different physical condition at low peptide concentrations (1-3 wt %). CD spectroscopy shows that at low pH or salt concentration the molecules are unfolded in a coil conformation and, thus, unassembled. However, gelation is observed at high pH values or at high salt concentrations (150 mM) where β-sheet secondary structure due to hairpin folding is observed. The intimate relationship between β-Hairpin molecule chemistry (sequence and turn), solution conditions and the consequent structure and viscoelasticity properties is discussed. The gelation kinetics, which can be tuned by temperature, salt concentration, and pH, are studied by dynamic oscillatory measurements. The hydrogels have a shear-thinning network that quickly recovers to the original state after cessation of shear. Hydrogel storage moduli (G') are in the order of kPa at low concentration of peptide (2 wt %) indicating significant gel rigidity. Importantly, the gel is also reversible with pH or temperature. As the pH of the gel is lowered molecules unfold and the G' of the gel drops drastically. It is also found that with the correct designs of the molecules and solution conditions sol-gel transition temperatures can be tuned. Laser Scanning Confocal Microscopy data reveals that hydrogel structure is heterogeneous at the microscale. The self-assembled regions, imaged by TEM consist of interconnected fibrillar/tubular networks. Small angle and ultra small angle scattering results are in accordance with the microscopy findings.

Wednesday 6:00 Reflections/Waterfront PO21

Investigating the local structural properties op MAX1(b-hairpin peptide) using multiple particle tracking microrheology

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We have used Multiple Particle Tracking (MPT) for making precise, dynamic, time evolving localized measurements of the structural properties of the MAX1 (b-hairpin peptide) gelation process. MAX1 exhibits pH

dependent intramolecular folding mechanism, forming hydrogels rich in b-sheet by self-assembly process, with storage and loss modulus increasing with gelation time. Using video microscopy, we have simultaneously measured the Brownian dynamics of fluorescent tracer particles embedded in the complex medium and interpreted their motions in terms of the transient local viscoelastic response. We have investigated the gelation dynamics as a function of MAX1 concentration. In addition, we report the effect of the size and chemical properties of the tracer particles on the transient local properties and also on the gelation time and mechanism.

Wednesday 6:00 Reflections/Waterfront PO22

High-bandwidth microrheology applied to solutions and networks of semiflexible biopolymers

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Semiflexible protein filament networks are characteristic of the cytoskeleton and the extracellular matrix, and their dynamics over a broad range of time and length scales are at the basis of cellular mechanics. We have developed one and two-particle microrheology, employing micron-sized embedded beads and laser trapping combined with interferometric displacement detection, to study the rheological properties of mono-disperse semiflexible fd-virus solutions. We have tested these relatively new techniques in well-known limits using fd virus as a model polymer. Concentrations tested spanned the dilute, semi-dilute and concentrated regimes allowing comparison with recent theoretical treatments of both the dilute low-frequency regime (rod diffusion) and the high-frequency single filament (internal) dynamics. We find good agreement in these limits and we also obtained data on collective dynamics in the entangled regime for which no theoretical model is yet available. Once proven as a reliable technique to characterize the micro-rheological behavior of uniform filament networks, particle tracking may be applied towards detection of subcelluar mechanics, motor activity, granular transport, etc.

Wednesday 6:00 Reflections/Waterfront PO23

Dynamic mechanical study of chitosan solutions

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Chitosan is a biopolymer partly deacetylted obtained by the alkaline treatment of chitin, a structural polysaccharide found in the exoskeleton of many arthropods and crustaceans. Chitosan becomes a positively charged polyelectrolyte in solution due to the protonation of the free amine groups in the molecule below a pH of 6.2. This natural biopolymer is recommended as a suitable functional material for pharmaceutical and biomedical applications due to its cationic character. Many studies have been focused on the effect of pH, salinity, degree of deacetylation (DDA) and molecular weight on the conformation of chitosan molecules in diluted solution. However, the dynamic mechanical properties of concentrated chitosan solutions have been scarcely studied. Thus, in this work, the rheological properties of concentrated chitosan solutions were characterized at 25°C in dynamic mode in linear viscoelastic regime. The effect of ionic strength on viscoelastic properties was investigated. Increasing ionic strength reduces the electrostatic repulsion force within positively charged chitosan molecules by screening effect resulting in a decrease of storage and loss moduli (G' and G''). The salt effect is explained in terms of Debye length and radius of gyration. Increasing chitosan concentration (C_{Chit}) increases the viscosity ($\eta_0 \sim C_{Chit}^{4.3}$). We found a relationship between chitosan concentration and the peak time (τ) of the relaxation spectra determined from G' and G''. The dependency of the peak time on C_{Chit} is ($\tau \sim C_{Chit}^{4.2\text{-}4.5}$). The power-law exponent is slightly dependent on the ionic strength.

Wednesday 6:00 Reflections/Waterfront PO24

Charge density effects in polyelectrolyte solution rheology

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Random copolymers of 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride (PMVP-Cl) in ethylene glycol (good solvent) with no added salt were studied over wide ranges of concentration and charge density using rheology. The quaternized polymers were prepared at a fixed degree of polymerization, but at various charge densities (0, 3, 10, 17, 42, 55 mole %). Experimental results show that the apparent viscosity is a function of both polymer charge density and concentration, and shear thinning was observed at high shear rates for polyelectrolyte solutions above the overlap concentration. The specific viscosity of a quaternized polymer solution increases with charge density in the semidilute unentangled regime except for the highest charge density (55 mole %), while in the high concentration regime the weakly charged polymer has the highest specific viscosity, which increases along a steep line with the same slope as the uncharged parent polymer. Condensed counterions on the polyions result in an upper limit of charge density which impacts the conformation and viscosity of polyelectrolytes. The reduced viscosity data are independent of concentration at low concentrations but depend on charge density making intrinsic viscosity of polyelectrolytes a function of charge density. Experimental data obey the Fuoss law ($\eta_{red} \sim c^{-1/2}$) in the semidilute unentangled regime. The relaxation time deceases with concentration in the semidilute unentangled regime (¦Ó ~ $c^{-1/2}$), is independent of concentration in the entangled regime and increases rapidly with increasing concentration at the highest concentrations studied.

Wednesday 6:00 Reflections/Waterfront PO25

Numerical simulations of structure formation in sheared nematic LCP

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We consider the Doi-Marrucci-Greco kinetic model, allowing a full coupling between flow structure, nematic director and order parameter distortions, and with imposed plate motion and molecular anchoring conditions. To do numerical simulations, we first expand the probability distribution function using the spherical harmonic functions, so to derive a system of partial differential equations about the amplitudes. Then 4th order finite difference methods are used for spatial discretizations. And spectral deferred correction is used in time integration to get high order solutions. We also incorporate the moving grid technique and adative time step size into the algorithm to promote the efficiency of the simulation. Numerical results are present to show flow structures for some parameter values of Ericksen number and Deborah number.

Wednesday 6:00 Reflections/Waterfront PO26

One and two point microrheology in wormlike micelle systems

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We have performed microrheology experiments using optical tweezers on wormlike micelle solutions. In these systems we expect the presence of the bead to have a negligible influence on the local micellar structure. This is confirmed from the good agreement, up to high frequency, between one-point and two-point microrheology. One and two point microrheology measure the local and bulk viscoelastic properties respectively. This result is further verified over the whole frequency range using a mechanical rheology technique. As expected in an incompressible fluid we measure and we observe a Poisson ratio of 0.5 using the two-point technique. Scaling of the correlation power spectra density with separation distance between the two beads is shown. We also show the existence of inertial effects, which lead to a turndown of the correlation spectra.

Wednesday 6:00 Reflections/Waterfront PO27

On the strength of monodomain attractors in sheared nematic polymers

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Employing a mesoscopic Doi tensor model, we study the transient properties of sheared nematic polymer monodomains consistent with typical experimental protocols. We begin with the flow-phase diagram of monodomain attractors versus nematic concentration (N) and Peclet number (Pe, shear rate normalized by average rotational relaxation rate). Our goal in this poster is to overlay on the phase diagram a statistical diagnostic of the expected time, $<t>_A$, to reach a small neighborhood of every attractor A. The statistics is taken over the arbitrary quiescent director angle on the sphere, modelling experiments that begin from rest. We use the linearized decay rates of all steady and periodic attractors for two purposes: to give a local measure of attractor strength, and to measure when the nonlinear flow has settled into a neighborhood of the attractor. In parameter regimes with multiple attractors, we perform statistics within the respective domain of attraction. The tools are developed first for confined in-plane orientation tensors, then extended to full tensor dynamics. Their comparison conveys which in-plane attractors are unstable to out-of-plane perturbations, and for those in-plane attractors which remain stable in the full space, whether the slowest tensor modes (which dominate $<t>_A$) are out-of-plane or in-plane. This measure of attractor strength is critical for any study of structure development in confined shear flow, since $<t>_A$ relative to the timescale of plate-generated distortions will determine whether the attractor is ever fully resonated.

Wednesday 6:00 Reflections/Waterfront PO28

Transient dynamics and rheology of sheared nematics polymers

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It is well-known that defects play a dominant role in the structure properties of nematic polymers and liquid crystals. Defects have been classified and rigorously analyzed in the context of the Leslie-Ericksen continuum theory, where the fundamental orientation variable is the norm one director field. In mesoscopic models, where the second-moment orientation tensor is the primary variable, defects are associated with degeneracy conditions defined in terms of the eigenvalues, or order parameters. Namely, when the largest eigenvalues collide, either in pairs or triplets, the peak direction of orientation is degenerate, and such states are called defects. Defects therefore exist even in bulk monodomains, and our purpose in this poster is to consider a model problem for in-plane, shear-driven, orientation tensor dynamics. We find that defect dynamics has a very surprising (to us) and tractable behavior. We classify the defect set into disjoint components, and show how the monodomain in-plane, global mesoscopic dynamics can be organized in terms of flow through the defect set. Comparisons with related kinetic simulations are also given. These idealized studies are intended as an insight into defect structures for which the second-moment tensor has defects in finite lengthscale structures.

Wednesday 6:00 Reflections/Waterfront PO29

Transient molecular orientation in the wagging regime of a poly(benzyl glutamate) solution

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The consequences of director tumbling at low rates in liquid crystalline polymer (LCP) solutions have been extensively studied via rheology and in situ measurements of molecular orientation. However, the 'waggging' regime anticipated by the Doi molecular theory has received considerably less scrutiny. Mewis and coworkers (Macromolecules, 30:1323, 1997) identified possible rheological signatures of wagging in ‘step-down’ experiments from high rates (in the flow-aligning regime) to intermediate rates. Characteristic organized oscillations in shear and normal stress occured over a narrow shear rate range located where theory anticipates director wagging. We have followed the protocols of Mewis and coworkers, and used synchrotron x-ray scattering and a fast detector (~60 milliseconds per image) to collect complementary data on the degree and direction of average molecular orientation during this type of step-down experiment. The structural response will be compared and contrasted with the previously identified mechanical signatures.

Wednesday 6:00 Reflections/Waterfront PO30

Orientation of platelets in multilayered nanocomposite polymer films

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The orientation of platelets in micron thick polymer-clay nanocomposite films was investigated by means of small-angle neutron scattering (SANS), small angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD). The films with various clay contents (15 % to 60 % by mass fraction) were prepared by a layer-by-layer approach from polymer-clay solutions which led to the formation of high degree of orientation in both polymer and clay platelet. Shear-induced orientation of polymer-clay solutions is compared with the orientation of polymer-clay films. SANS, SAXS, and WAXD, with beam configurations in and perpendicular to the spread direction of the film, were used to determine the structure and orientation of platelets. In all films, the clay platelets orient preferentially in the plane of the film. The observed differences in semi-dilute solutions, with clay surface normal parallel to the vorticity direction versus bulk films, with clay surface normal parallel to the shear gradient direction at clay mass fractions of 40 % and 60 % are attributed to the collapses of clay platelet during the drying process.

Wednesday 6:00 Reflections/Waterfront PO31

Shear gelation and relaxation of polymer-clay dispersions

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Reversible shear induced gelation of semi-dilute aqueous colloidal dispersions consisting of monodisperse discoid particles (Laponite) and weakly interacting polymer (polyethylene oxide) is studied through a combination of small angle neutron scattering and oscillatory shear. When shaken the samples undergo a dramatic transition from low viscosity fluid to a self supporting turbid gel. This complex non-linear behavior is found to occur over a narrow composition regime near a composition commensurate with saturation of the clay surface with polymer. Based on SANS and rheology, shear gelation is found to occur through the deformation of large stable flocs that allows an increase in polymer bridging. The temporary macroscopic flocs formed through flow slowly breakup with polymer desorption. The shear induced gelation is time reversible and strongly temperature dependent suggesting that relaxation is an activated process. Samples showing shear induced gelation are also able to form stiff stable gels which are characteristically similar to pure clay dispersions.

Wednesday 6:00 Reflections/Waterfront PO32

Rheological properties of polystyrene /clay nanocomposites prepared by in-situ free radical polymerization

Yu Zhong and Shi-Qing Wang
Polymer Science, The University of Akron, Akron, OH 44304

By using a mixture of commercial alkyl chain surfactant and surfactant containing a C=C group to modify the montmorillonite clay surface, exfoliated PS and PMMA/clay nanocomposites were obtained. The exfoliated structure was verified by both transmission electron microscopy (TEM) and X-ray diffraction (XRD). The thermogravimetric analysis (TGA) reveals that the degradation temperature increases above 50 °C compared with the pure matrix. The rheological behavior of such exfoliated polystyrene (PS) and poly(methyl methacrylate) (PMMA)/nanoclay composites were explored. These samples and their rheological properties are all stable even after subjected to 300 °C for a long time. At all clay loadings from 4 to 9 wt. %, the samples display high elasticity at all temperatures up to 300 °C, suggesting strong networking among the nanoclay particles. The stress relaxation behavior of the nanocomposite reveals new insight into the reinforcement mechanism and the Payne effect.

Wednesday 6:00 Reflections/Waterfront PO33

Rheology of single-walled carbon nanotube/PMMA nanocomposites

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The rheology of single-walled carbon nanotubes (SWNTs)/poly(methyl methacrylate) (PMMA) nanocomposites was investigated using linear viscoelastic measurements in oscillatory shear with small strain amplitudes. The shear modulus and viscosity of the nanocomposites increase with the addition of nanotubes. At low frequencies, the storage modulus of the nanocomposites versus nanotube content exhibits a typical percolation behavior. The nanocomposites with high nanotube loadings undergo a glassy, transient, first rubbery, first terminal, second rubbery, and a second terminal region. The second rubbery plateau can be attributed to a nanotube network formed in the composites. It is also found that the second rubbery plateau diminishes when the nanotubes are aligned in the composites.

Wednesday 6:00 Reflections/Waterfront PO34

Non-linear melt rheology of carbon nanotubes/polypropylene nanocomposites: Elasticity and negative Weissenberg numbers

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The role of multi-wall carbon nanotubes (MWNT) on the viscoelasticity of MWNT/Polypropylene (PP) nanocomposites was studied using dynamic and steady shear measurements. The content of the nanotubes ranges from 0.25 % vol. to 15 % vol. Compared to pure PP, the nanocomposites exhibit stronger shear thinning behavior and the critical strain describing the linear viscoelastic region plummets with increasing nanotube content. On time scales larger than the longest relaxation time of the polymer, the nanocomposites become highly elastic and when the tube content exceeds 1 % vol. fraction, they develop "solid-like" behavior, consistent with a network structure. The time-temperature superposition as well as the Cox-Merz rule fails suggesting that the temperature dependence of the nanotube microstructures is significantly different from that of the PP and that the nanotubes are interconnected. Remarkably, we find a large negative first normal stress difference when the volume fraction exceeds 1% with Weissenberg numbers ranging from -2.5 to -35. The absolute value of the first normal stress difference increases with concentration at a given shear rate.

Wednesday 6:00 Reflections/Waterfront PO35

Rheology of poly-methacrylate glasses

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A cooperative mechanism is invoked to explain the acute property changes observed in poly-methacrylate liquids near the glass transition temperature. This theory implies the existence of cooperatively rearranging regions (CRR) as characterized by a dynamic length scale, which is observed both in experiments (NMR and probe diffusion) and computer simulation. Armed with the 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. This scaling model is applied to both oscillitory shear and dielectric data for poly(*n*-butyl methacrylate, poly(*n*-hexyl methacrylate), and poly(*n*-octyl methacrylate). The rheological consequences of this model will be discussed for both equilibrium and non-equilibrium states.

Wednesday 6:00 Reflections/Waterfront PO36

Description and validation of a nonlinear viscoelastic theory for glassy polymers

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We will present a thermodynamically consistent, nonlinear viscoelastic model of glassy polymers that accurately predicts enthalpy relaxation, volume recovery, physical aging, and yield in tension and compression over a temperature range of T_g±120°C and pressures up to 2kbar using one parameter set for all tests. Moreover, all model parameters are uniquely defined by clear physical measurables. Derived as an expansion in the free energy, second order terms are related to the moduli, CTE, and heat capacity at T_g. Third order terms are necessary if such phenomena as the temperature dependence of the CTE or the heat capacity are desired. Even the pressure dependence of T_g and the viscoelastic shift factor are predicted naturally and accurately. Four unfilled polymers (three epoxies and one thermoplastic) and four filled polymers (silica, alumina, and glass microballoons) have been characterized and evaluated. Good agreement is seen for all systems on all tests using one constant set of parameters for each system. The formalism is, in form, similar to thermorheologically simple linear viscoelasticity with two exceptions. The Hencky finite strain measure is employed, and the material clock depends on the potential energy of the system rather than simply temperature as in its WLF limiting form.

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 6:00 Reflections/Waterfront PO37

Torque and normal force measurements in polymer glasses

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The torque and normal force responses of polymeric glasses have been shown to provide a rich array of information concerning the nonlinear viscoelastic response of these materials. In particular, past work showed that while most glassy polymers have torsional moduli that are the same within about 25% of 1 GPa, the normal force responses seem to show much larger differences with, for example poly(methyl methacrylate) (PMMA) showing a normal force that is approximately 3 times that of polycarbonate at the same strain and for the same sample geometry. The purpose of the present work has been to investigate whether or not the origins of these large differences are related to specific molecular level mechanisms. In particular, we are investigating how the first sub-glass transition relaxation (beta-relaxation) affects the normal force response. This is done by examining a series of n-alkyl methacrylates for which the b-relaxation is relatively constant but the alpha-relaxation decreases as side-chain length increases hence moving the two relaxations closer together. Results from our present experiments indicate that the cross over region between alpha-relaxation and the beta-relaxation does have a major effect on the normal force response when comparing poly(methyl methacrylate) with poly(ethyl methacrylate). The poster will include further results on the normal force of polymers with different interactions between alpha and beta-relaxations as well as different heights in their beta-relaxations.

Wednesday 6:00 Reflections/Waterfront PO39

Effects of the degree of undercooling on flow-induced crystallization in polymer melts

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Flow-induced crystallization (FIC) models share the common physical intuition that flow induces local orientations of polymer chains, thus enhancing the nucleation rate. Under this respect, temperature is expected to be an important factor in determining the chain degree of orientation. Higher temperatures, which determine shorter relaxation times, would imply smaller orientations. At the same time, temperature is also the key parameter in quiescent crystallization kinetics. As a consequence, a significant coupling between temperature and flow, even under isothermal conditions, is expected. This relevant point has never been explicitly considered in FIC models.

In this work we show how the Doi-Edwards micro-rheological model, coupled to classical models for the quiescent nucleation rate, can be used to describe combined temperature and flow effects on the early stages of polymer isothermal crystallization. First, experimental data that clearly demonstrate the combined effects of temperature and flow on crystallization kinetics are presented. Then, the Doi-Edwards-based FIC model is implemented to quantitatively describe the observed experimental behaviour.

Wednesday 6:00 Reflections/Waterfront PO40

Influence of long chain branching on elongation and shear properties of polyethylene

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This paper reports the influence of long chain branching on the processability of molten polethylenes in 2D planar elongation slit flow. The effect of long chain branching in two commercial grade, metallocene catalysed, linear low density polyethylenes with nearly equal molecular weights were characterised. Flow birefringence experiments were carried out to determine the centreline principal stress difference of two polymers. It was observed that stress builds up slowly in the case of more branched polyethylene while the maximum stress appears at the slit entrance for the less branched polyethylene all the flow rates considered. These results are consistent with oscillatory shear viscoelastic and steady shear experiments which indicate that higher levels of branching retards the moduli and zero shear viscosity.

Wednesday 6:00 Reflections/Waterfront PO41

Structural formation of amorphous poly(ethylene terephthalate) under uniaxial deformation

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An in-situ study of structural formation of amorphous poly(ethylene terephthalate) (PET) during uniaxial deformation above its Tg (90 oC) was carried out by wide-angle X-ray diffraction (WAXD). Results indicated that the relationships between structure and mechanical property can be divided into three zones: I, II and III. In Zone I, the oriented mesophase is induced by strain, where the applied load remains about constant. The mesophase is the precursor structure of crystallization. In Zone II, crystallization is initiated from the mesophase through nucleation and growth, where the load starts to increase marking the beginning of the strain-hardening region. The initial crystallites are defective but they form an effective three-dimensional network to enhance the mechanical property. The perfection of the crystal structure and the orientation of the crystals all increase with strain in Zone II. At the onset point of Zone III, the ratio between load and strain is about constant, while the stable crystal growth process takes place until the breaking of the sample. An increase of the molecular weight was found to enhance the overall mechanical properties including the load to induce the mesophase and the sample strength before it broke. Recent results from in-situ studies using small-angle X-ray scattering (SAXS) and Raman spectroscopy will also be presented.

Wednesday 6:00 Reflections/Waterfront PO42

Rheological effects in reactive blending of polymers

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Thermoplastic vulcanizates (TPV) based on polyethylene (PE) and copolymer of ethylene and vinyl acetate (EVA) were dynamically crosslinked in a batch mixer. The vulcanization was carried out in the presence of the crosslinker agent tetrapropoxysilane (TPOS) and of the organometallic catalyst dibutyl tin oxide (DBTO). Phase inversion occurred during the reactive mixing, i.e. the EVA major phase, initially the matrix, was finally dispersed in the PE minor phase. Such blends exhibit the processing properties of thermoplastics due to the matrix of PE, and the characteristics of elastomers due to the high content of crosslinked EVA. The properties of these blends depend of the degree of the dispersion of the EVA in the PE, which is determined by the viscosity, elastic ratio and interfacial tension between the components. The aim of the study was to understand how the rheological properties of both components and the processing conditions control the phase inversion and affect the final properties. The morphology of reactive and nonreactive blends was determined via scanning and transmission electron microscopy after extraction of the EVA phase with boiling toluene. The linear viscoelastic properties of the blends were determined using a parallel plate rheometer. The torque of the mixer was also used to follow the evolution of the viscosity during the reaction. The effects of temperature and rotational speed of the mixing rotors were studied to obtain the finest morphology. A plateau was observed in the evolution of the torque of the mixer during the reaction and it was related to phase inversion. The use of a low viscosity PE was found to favor phase inversion due to a more favorable viscosity resulting in a finer morphology of the elastomeric phase.

Wednesday 6:00 Reflections/Waterfront PO43

Rheological response of isotactic polypropylene/polyamide-6 blends during coalescence

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The rheological response of coalescing blends of isotactic polypropylene (PP) and polyamide-6 (PA6) was studied in a cone and plate rheometer at shear rates in the range of 0.1 - 0.5 1/s. A simple model for coalescence was developed to provide kinetic features of the phenomena, which was also used to analyze experimental results. The pre-coalescence droplet morphology was created by melt blending the polymers in a twin-screw extruder at several compositions and was subjected to a simple shear flow in a cone and plate rheometer. The rheological data was analyzed after removing the effects of viscosity mismatch to leave only the interfacial effects of coalescence. It was found that the decrease of interfacial area due to coalescence produced a build up of the shear stress with time, which showed strong correspondence with the interfacial stress. Semiquantitative agreement was found between the experimental findings and the theoretical predictions from Lee and Park model (J. Rheol. 38:5 1405-21, 1994).

Wednesday 6:00 Reflections/Waterfront PO44

Yield-like constitutive transition in entangled melts

Prashant Tapadia and Shi-Qing Wang
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In this work we extend our previous investigation of the fast flow behavior of entangled solutions to include entangled melts. As the first step, we study the flow behavior of binary mixtures made of an ultra high molecular weight polymer dispersed in a series of matrices that are also entangled. By varying the matrix molecular weight, we can dial the onset of the upper branch to provide different conditions to determine when a stress-induced transition is possible from the entangled to a disentangled state. The second variable affecting the terminal plateau width of entangled binary mixtures is the composition, which is also varied to elucidate the dominant features of the non-analytical constitutive behavior of entangled polymers. These results offer new insight into such common phenomena as shear thinning.

1. P. Tapadia and S. Q. Wang, “Constitutive transition in strong flow of entangled polymeric fluids”, to be presented in as Paper EA2 on Tuesday at 10:10 AM.

Wednesday 6:00 Reflections/Waterfront PO45

Rheological behavior of etylene vinyl acetate copolymer with vinyl acetate and dicumyl peroxide contents

Yu-taek Sung, Won Jin Seo, Jung Hoon Park, and Woo Nyon Kim
Chemical and Biological Engineering, Applied Rheology Center, Korea University, Seoul 136-701, Republic of Korea

Rheological and thermal properties of ethylene vinyl acetate copolymer (EVA) were studied by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). The samples of EVA varying the vinyl acetate (VA) and dicumyl peroxide (DCP) contents were prepared by screw extrusion. For the EVA (26 wt% VA content) containing 0 phr DCP as a crosslinking agent, the storage modulus showed higher than those of the EVA (26 wt% VA content) containing 0.5, 1.0, 1.5, and 2.0 phr DCP. The crystallization temperature was decreased from 48.6 °C to 41.0 °C for the EVA (26 wt% VA content) containing 0.0 and 2.0 phr DCP, respectively. However, the glass transition temperature did not change significantly with the DCP. From the results of the above DMTA and thermal analysis, it is thought that the crosslinking effect of the EVA with the DCP is not significant. From the DMTA result of EVA with VA content, the storage modulus was decreased with the increasing the VA content in the EVA, and the sample of EVA became flexible with the increasing of the VA content. From the study of thermal analysis and DMTA, it is suggested that the crystallinity of the EVA decreases with the DCP, and also the chain flexibility of the EVA is mainly influenced by the crystallinity of the EVA.

Acknowledgment: This study was supported by research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University, Seoul, Korea.

Wednesday 6:00 Reflections/Waterfront PO46

Rheology of polyethylenes with novel branching topology

Rashmi Patil[1], Ralph H. Colby[1], Guanghui Chen[2], and Zhibin Guan[2]
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[2]Department of Chemistry, University of California, Irvine, CA 92697

Ethylene pressure was used to vary the molecular architecture of amorphous polyethylenes synthesized with palladium bisimine catalysts. At low ethylene pressure (0.1 atm), densely branched polymers are formed and their melt rheology indicates no entanglement even though the weight-average molecular weight is 370000. Polymers produced at higher ethylene pressures (1 atm and 500 psi) have only slightly higher molecular weights, but show entanglement effects in their rheology. As ethylene pressure is increased, the polymers are more sparsely branched. NMR suggests similar levels of short-chain branching (92-97 branches per 1000 carbons) in all three samples. The large-scale architectural differences in long-chain branching structure account for the rheological features in these branched polyethylenes.

Wednesday 6:00 Reflections/Waterfront PO47

Enhanced melt strength and stretching of linear-low density polyethylene extruded under strong slip conditions

Teresita de Jesús Guadarrama-Medina, José Pérez-González, and Lourdes de Vargas
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The effect of extrusion under strong slip conditions on the extensional properties of linear low-density polyethylene (LLDPE) was studied in this work. Pure LLDPE and LLDPE with a flouropolymer polymer processing additive (FPPA) were extruded in a capillary rheometer and then elongated under uniaxial tension with a "Rheotens" device. The pure LLPDE did not exhibit slip while the FPPA promoted strong slip in the die, which was evident through the elimination of flow instabilities, electrification of the extrudates and decrease in die swell. Different pressures, temperatures and die diameter were considered in this study. Our results indicate that LLDPE extruded under strong slip conditions exhibits enhanced strength and drawability in extension as compared to the case in which slip is absent. In addition, the difference in the melt strength and draw ratio between both processing conditions increased along with temperature and slip velocity.

Wednesday 6:00 Reflections/Waterfront PO48

Rheological characterization of structural evolution in triblock copolymers

Amy Philips and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH

This work focuses on extending the existing rheological methods used to characterize the order-disorder transition (ODT) in block copolymers. The structural transitions in several systems of polystyrene-block-polyisobutylene-block-polystyrene (PS-PIB-PS) and polystyrene-block-polyisoprene-block-polystyrene (PS-PI-PS), with differing morphology and molecular weight, are studied using steady and oscillatory shear rheometry and capillary rheometry. Below ODT, these samples not only exhibit solid-like viscoelasticity in small amplitude oscillatory shear measurements, but due to the long range order in the triblocks, they also show yield-like shear thinning in steady shear measurements in the controlled stress mode. This yield-like shear thinning occurs at a progressively lower applied stress as the experimental temperature rises closer to the ODT. At the conventionally determined ODT temperature, taken as the onset of the terminal behavior in oscillatory shear, creep experiments indicate that the structural evolution of the block copolymers is not universal, as evidenced by a persistent yield-like shear thinning in some systems. For these systems at ODT temperature shear thinning remains evident from the small amplitude oscillatory shear even though the system shows terminal behavior (i.e. $G'' > G'$). Thus, the more systematic analysis, based on oscillatory shear measurements and new creep experiments, indicates the presence of residual ordered structures for some systems. Above ODT temperature, the oscillatory shear measurements further indicate that mesostructures, larger than individual chains, are still present because the onset of shear thinning occurred sooner in the materials than expected for homogeneous molecularly disordered melts. A combination of oscillatory shear and creep tests is shown in this work to provide a more detailed characterization of the evolution between ordered and disordered phases in ordered materials such as block copolymers.

Wednesday 6:00 Reflections/Waterfront PO49

LAOS (Large Amplitude Oscillatory Shear) behavior of PEO-PPO-PEO triblock copolymer solution

Kyu Hyun, Kyung Hyun Ahn, and Seung Jong Lee
Chemical Engineering, Seoul National University, Seoul 151-744, Republic of Korea

Rheological properties of PEO-PPO-PEO triblock copolymer solution under large amplitude oscillatory shear (LAOS) have been investigated. PEO-PPO-PEO triblock copolymer undergoes a transition from sol to gel with the increase of temperature. This transition is caused by the dramatic change of microstructure. From the results of temperarture sweep test, we observed three regions: sol, soft gel, and hard gel. Change of the microstructure with temperature affects LAOS behavior. First, sol region showed Newtonian type. Second, soft gel region showed combination of type I (G', G'' decreasing) and type IV (G', G'' increasing followed by decreasing). Third hard gel region showed type III (G' decreasing, G'' increasing followed by decreasing).We have also obatained the stress curve using high performance ADC (anolog digital converting) card.

Wednesday 6:00 Reflections/Waterfront PO50

Spreading of model non-Newtonian fluids

Gitanjali K. Seevaratnam, Lynn M. Walker, and Stephen Garoff
Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

The aim of this study is to systematically characterize the effects of fluid elasticity on the motion of liquid-vapor interfaces near contact lines. This is an important step in modeling and understanding spreading of non-Newtonian fluids. We create a well-defined interface for investigation by forcing a Pyrex rod into a beaker of the test fluid at controlled rates. The test fluids are a series of polystyrene-based Boger fluids of increasing elasticity. These viscous fluids exhibit the lack of shear-thinning and large first normal stress differences characteristic of Boger fluids. The test fluids are used to characterize dynamic wetting under a forced disturbance applied by the Pyrex rod. Experiments show that even the most weakly elastic of these fluids deviate from the viscous bending behavior observed previously for Newtonian fluids. The more elastic fluids show increasingly drastic deviations from the Newtonian interfaces. These deviations are described and attempts to explain the novel interface shapes made based on the elastic behavior of the test fluids.

Wednesday 6:00 Reflections/Waterfront PO51

Multiplicity and stability analysis of the nonisothermal film blowing process

Hyun Wook Jung, Joo Sung Lee, and Jae Chun Hyun
Dept. of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea

The multiplicity and stability of the nonisothermal film blowing process have been investigated solving the governing equations of the system with a Phan-Thien and Tanner viscoelastic fluids. A newly-devised transient numerical scheme based on OCFE (orthogonal collocation on finite elements) has been employed in this study to produce the first transient solutions to date, which are hitherto difficult to obtain due to severe numerical problems caused by the inherent nonlinearity involved in the dynamics of the film blowing process, especially when the system is in oscillatory instability known as draw resonance. Several other important mathematical schemes have also been incorporated into the modeling equations including the coordinate transformation of the independent variables. The effects of various process conditions such as viscoelasticity and cooling on the multiplicity and stability have been theoretically examined and successfully compared with experiments. Thus obtained results make possible more systematic analysis of the process including the draw resonance criterion based on the traveling times of kinematic waves and the development of novel stabilizing devices such as draw resonance eliminator. These theoretical results about the process stability are quantitatively confirmed by comparing with experiments.

Wednesday 6:00 Reflections/Waterfront PO52

Stability analysis of the film casting process with encapsulation die

Joo Sung Lee, Hyun Wook Jung, and Jae Chun Hyun
Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea

A film casting simulation has been used to demonstrate why the encapsulation extrusion process is so effective industrially in enhancing the stability of the extrusion. Like the draw resonance eliminator, the ingenious device called encapsulation dies is introduced to reduce neck-in and stabilize polymer melts for extrusion coating process. In coextrusion, the high-melt-strength resin (e.g., LDPE) will often make possible the film casting of low-melt-strength resins like HDPE and LLDPE by being extruded on the outer edge of the core film, i.e., encapsulating the core material. The encapsulation extrusion process exhibits minimal neck-in in cast film while offering excellent draw properties and web stability for uniform coating, an important productivity improvement in paper coating process. In this study, we explain why the encapsulation extrusion method is so successful in stabilizing the draw resonance in extrusion coating process. The simulation method of the present study can be used to explain the reasons behind their success and also help to find other ways to accomplish such stabilizing results.

Wednesday 6:00 Reflections/Waterfront PO53

Microrheology of elastomeric polypropylene probed by rheo-optical FTIR spectroscopy

Rajyalakshmi Inapagolla[1], Rangaramanujam Kannan[1], Wily Wiyatno[2], Gerald G. Fuller[2], and Robert Waymouth[2]
[1]Chemical Engineering, Wayne State University, Detroit, MI 48202; [2]Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Tacticity plays a key role on the structural, mechanical and physical properties of polymers. With metallocene catalysis, it is possible to synthesize polymers with varying degrees of isotacticity. This study investigates the molecular and microstructural origins of the complex deformation response of elastomeric stereoblock polypropylene (ePP-10), containing isotactic and atactic fractions. This ePP-10 can be solvent extracted into ether soluble (ES), heptane soluble (HS) and heptane-insoluble (HI) fractions of increasing meso pentad content. In e-PP, there is a non-uniformity in the isotactic segment length, which leads to crystallites of varying sizes, resulting in a lower crystallinity. Hence its material properties are intermediate between highly isotactic and atactic polypropylenes.

The deformational response of polymer microstructure and its influence on the material property changes can be better understood from rheo-optical experiments. Rheo-optical FTIR spectroscopy is a versatile tool that can characterize simultaneously, the individual component responses in both semi-crystalline homopolymers and blends. The IR absorbance spectra of ePP and its fractions showed the subtle differences, reflecting greater helical chain content in the highly isotactic fraction and less crystallinity in the low isotactic fractions. Upon uniaxial tensile deformation to great than 300%, ePP-10 exhibits strain-induced morphology changes, resulting in increased helical content and mesophase formation. This deformation-induced transformation is most strongly evident in the HS fraction. The orientation dynamics of the solvent fractionated polymers most nearly reflect those of homopolymers with similar tacticity: HS behaves comparably similar to the parent ePP-10, HI to highly isotactic PP and ES to atactic PP. The rheo-FTIR findings agree well with the WAXD, SANS and birefringence data of Wiyatno et al.

Wednesday 6:00 Reflections/Waterfront PO54

Conformational evolution of polymer chains over extended time periods and polymer lengths

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

Knowledge of the conformational evolution of a polymer chain provides invaluable information for all polymer properties, including stress and birefringence. Unfortunately, the chain evolution is usually determined by monitoring single beads for short times only (i.e. for periods much shorter than those of the polymer stress), due to shortage of appropriate configuration functions. In this talk we present the configuration evolution for the same extended time periods and polymer lengths as our computational results for the polymer stress. We achieve this by employing proper conformational functions and applying appropriate scaling laws. Results of Brownian Dynamics simulations of semiflexible polymers both far from and close to equilibrium will be presented which reveal the polymer evolution over more than twenty time decades, for polymer lengths varying from a few up to 100,000 beads.

In the talk, we show that knowledge of the conformational evolution over the complete set of time scales affecting a problem help us understand the polymer behavior without the need to use (approximate) theories for which the range of validity is not well known. Thus, we expect that the methodology we developed for monitoring the polymer configuration should have wide applications in the study of polymer rheology.

Wednesday 6:00 Reflections/Waterfront PO55

Integral model simulations of stress distributions in an axisymmetric stagnation flow

Jason Bryant and Wesley Burghardt
Northwestern University, Evanston, IL

We revisit steady axisymmetric flow birefringence data of Li et al. [JNNFM, 74, 151 (1998)] in connection with flow simulations of integral constitutive equations. The birefringence data were collected on a shear-thinning polystyrene solution in pressure driven flow past an axisymmetric stagnation. Depending on the flow direction, a forward or rear stagnation point is generated, dominated by either equibiaxial or uniaxial stretching. In this respect, axisymmetric flow birefringence provides greater kinematic complexity than that afforded by traditional applications of birefringence in 2-D planar geometries. We have previously used these data to test viscoelastic flow simulations of nonlinear differential constitutive equations. Relative to differential models, standard nonlinear integral constitutive equations offer the advantage that their uniaxial elongational predictions may be adjusted without any changes to their shear predictions. They are thus well-suited for isolating the impact of changing elongational predictions on the resulting stress distributions. Here we will present comparisons of axisymmetric birefringence data with computations based on Luo & Tanner's modification of the Papanastasiou, Macosko & Scriven model.

Wednesday 6:00 Reflections/Waterfront PO56

A mesoscopic description of diffusion process through polymeric materials

Quan Liu and Daniel De Kee
Chemical Engineering, Tulane University, New Orleans, LA 70118

Fick’s laws have been widely used to describe diffusion processes. For diffusion through complex polymeric materials, Fick’s laws can not always provide a quantitative description of the mass transfer process. An experimental setup to test the permeation through thin membranes under uni- or biaxial mechanical deformation has been built and will be described. Diffusion tests involving rubber, LDPE and layered- nanocomposite membranes will be discussed. Microscopic characterizations have also been performed to elucidate the structure of the polymeric materials. A mesoscopic theory is used to model the diffusion process of a simple solvent through a complex polymeric material. After choosing the state variables, the Poisson bracket and GENERIC formulation are applied and the governing equations describing the diffusion process are derived. Quantitative predictions and experimental data on the diffusion of acetone through natural rubber, as well as other systems will be presented.

Wednesday 6:00 Reflections/Waterfront PO57

Accurate numerical simulation with essential reduced-order microstructure models

Vidya Venkataramani, Radhakrishna Sureshkumar, and Bamin Khomami
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Flow modeling of dilute polymer solutions has been a subject of extensive research. Although continuum-level models can provide semi-quantitative description of the macroscopic viscoelastic stress, they contain little information on the microstructure. Brownian dynamics simulations (BDS) based on realistic micromechanical descriptions of polymer chains (e.g. nonlinear multi-bead spring models) can provide accurate information on the microstructure. However, incorporation of BDS into flow simulations can be prohibitively expensive or often infeasible for non-homogeneous flows. Hence it is desirable to develop computationally tractable models that contain accurate microstructural information while capable of predicting the kinematics in non-homogeneous flows. Recent experimental findings show that the vast majority of the molecular conformations under flow can be classified into a finite number of configurations such as fully extended states, dumbbells, half-dumbbells, kinks, folds and coils. Motivated by this, we develop a computationally tractable approach based on "configuration sampling", i.e., the configurations obtained from BDS are classified to get essential, reduced-order models that describe the probability of occurrence of a given configuration and how it depends on the strain rate. The overall stress is expressed as the sum of the stress contributions from a few (O(1)) configuration states rather that over thousands of trajectories. This information is subsequently used in flow simulations. The application of this method to the simulation of non-homogeneous flows of biological and synthetic polymer solutions will be demonstrated.

Wednesday 6:00 Reflections/Waterfront PO58

Effect of flow field on polymer chain scission in extensional and turbulent flows

Siva A. Vanapalli, Mohammad T. Islam, and Michael Solomon
Chemical Engineering, University of Michigan, Ann Arbor, MI 48109

The molar mass and molar mass distribution of polymers subjected to chain scission in planar elongational flow are profoundly affected by the inertial character of the flow, as quantified by the Reynolds number. The degradation of dilute polyethylene oxide (PEO) chains in aqueous based solvents of varying viscosity was quantified in the planar elongational flow of a cross-slot flow device by gel permeation chromatography with multi-angle laser light scattering detection. The scaling relationships for the steady-state molar mass with the applied strain rate were developed. Two different scaling exponents were observed depending upon the Reynolds number regimes. Differences of this kind, first quantified by comparing results from stagnation point elongation flows and contraction flows, have previously been attributed to different molecular mechanisms of scission [Odell & Keller, 1986; Nguyen & Kausch, 1992]. Yet, our observations in different Reynolds number regimes suggest a continuum fluid mechanics explanation for the difference in steady-state scaling exponent. Measurements of pressure drop across the cross-slot flow support this alternative hypothesis. Similar experiments of polymer chain scission in turbulent pipe flow were conducted. In this case a different exponent was found for the scaling of wall shear rate with steady-state molar mass. The implications of these different scaling exponents for polymer turbulent drag reduction will be discussed.

Wednesday 6:00 Reflections/Waterfront PO59

Molecular dynamics of a polymer tethered to a solid surface in a flow

Yannick Gratton and Gary W. Slater
Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

The dynamics of a single DNA molecule tethered to a solid surface in a shear flow has been observed experimentally by Doyle *et al*. They found that the polymer undergoes a recirculating motion due to a coupling between the flow pattern and the thermal fluctuations of the molecular conformations. Using Molecular Dynamics computer simulations with explicit hydrodynamic interactions, we examine the dynamical properties of a freely jointed chain (FJC) in similar conditions (i.e., confined between two surfaces). The time dependent chain extension and its variance are examined. We observe a similiar cyclic motion to that observed experimentally. We also examine finite size effects by decreasing the distance between the upper and lower surfaces to within a few solvent particle diameters.

Wednesday 6:00 Reflections/Waterfront PO60

Tensile properties and structure of topological gel: Molecular dynamics study

Fumio Sawa[1], Tetsushi Okamoto[1], Takeshi Aoyagi[2], Jun-ichi Takimoto[3], and Masao Doi[3]
[1]Power & Industrial Systems R&D Center, Toshiba Corporation, Yokohama 230-0045, Japan; [2]Analysis & Simulation Center, Asahi Kasei Corporation, Fuji, Shizuoka 416-8501, Japan; [3]Computational Science and Engineering, Nagoya University, Nagoya, Aichi 464-8603, Japan

We investigated tensile properties and structure of topological gel by molecular dynamics simulation. Topological gel (Okumura and Itoh, 2000) is quite different from conventional chemical gels and it has significant properties such as high transparency and good tensility. This new type of gel has sliding closslinks that can move along polymer chain. It was thought that they act like a pulley to keep the tension of polymer chains uniformly and cause the significant properties of topological gel. To clarify the pulley effect in topological gel, coarse-grained molecular dynamics simulations were performed by using COGNAC (http://octa.jp). For modeling the topological gel, linear molecules wrapped by circular molecules were set in a unit cell and gelation process in which sliding closslinks were formed by connecting the circular molecules at each other was proceeded. We also modeled the chemical gel which has non-sliding crosslinks by connecting the circular molecules and the linear molecules. After gelation, tensile deformation was applied to the modeled gels. Stress-Strain behavior and local structure of the topological gel were compared with that of the chemical gel. It was confirmed that topological gel has higher tensility than chemical gel. And they showed much different structure under tensile stress, while they seemed to be similar before deformation.

Wednesday 6:00 Reflections/Waterfront PO61

Multi-decade viscosity analyses during chemical and thermoreversible gelation, using Brookfield viscometers or rheometers and a novel control algorithm

David J. Moonay
Brookfield Engineering Labs., Inc., Middleboro, MA 02346

A novel algorithm was developed and successfully used in Brookfield DVLoader(TM), Wingather(TM), Rheoloader(TM) and Rheocalc(TM) software to control Brookfield viscometers and rheometers. It allowed multiple decades of apparent viscosity data to be acquired during (1) chemical and (2) thermoreversible gelation in both isothermal and cooling analyses of molecularly distinct systems. KRATON(R) 1650/Paratherm LR(TM) solutions were monitored during cooling from 100 to approximately 40 °C. 300-Bloom gelatin - 14 wt % in water - was studied during cooling from 50 to 30 °C. Isothermal chemical gelation of 1:1 wt/wt EPON(R) 828/EPI-KURE(R) 3046 mixtures was studied at 23, 50 and 60 °C. Apparent viscosities measured during one 23 °C cure experiment ranged from approximately 8.70×10^2 to 5.40×10^7 cP, for example. Data superimposibility indicated good repeatability of data for different reaction mixtures prepared with similar stoichiometry. Viscosities measured at approximately 10^4 seconds differed by 0.6 %, for example. This new algorithm, when used with Brookfield instrumentation for automated data acquisition and control, may prove useful to various laboratories that require automated monitoring of gelation but cannot afford more expensive or exotic equipment. Furthermore, this is a significant improvement over existing low-cost methods such as “torsion gelometers” that only provide gel times but no rheological data. This addresses, therefore, explicit needs of customers in different industries. Various aspects of the algorithm and its implementation are discussed in this poster.

Wednesday 6:00 Reflections/Waterfront PO62

A new integrated Rheo Small Angle Light Scattering (Rheo-SALS) device

Joerg Laeuger[1] and Gerhard Pfeifer[2]
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Small Angle Light Scattering (SALS) is a widely used technique for investigations of micrometer sized structures. In a SALS setup the light of a laser is directed onto the sample and the scattered light at small angles is then detected by a 2-dimensional detector. SALS gives information on the structure averaged over the whole scattering volume. Light scattering like other scattering methods, i.e. X-ray or neutron scattering, measure an intensity distribution in the so-called momentum space. This means large structures show scattering to small angles whereas small structures lead to scattering at large angles. SALS has been used frequently in combination with applied flow field to investigate structural changes induced by flow. However, a combination of a SALS setup with a state of the art

rotational rheometer (Rheo-SALS) would be more suitable for detailed investigations on structure-property relationships of complex fluids. A variety of such devices have been designed at several University laboratories. However, to make Rheo-SALS methods more commonly available a new device has been developed. It consists of a SALS module which can be easily adapted to a commercially available rheometer. The SALS module itself uses a laser diode as light source. The laser diode is mounted together with a prism and a polarizer directly onto a rheometer flange. Located on the same flange a temperature controlled measuring chamber is mounted. Concentric cylinder or parallel-plate geometries can be used. The scattered light within an angle of 11° is collected by an optical lens system and directed onto a screen. A beam stop removes the unscattered primary beam. The scattering patterns on the screen are recorded by a CCD camera. Details of the new Rheo-SALS device as well as simulation results on the performance of the optical lens system and first experimental results are presented.

Wednesday 6:00 Reflections/Waterfront PO63

Development of a combinatorial rheometer for polymer formulations

Howard J. Walls[1], Robert F. Berg[2], Alamgir Karim[1], and Eric J. Amis[1]
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The development of competitive formulations in the coatings and surfactant industries frequently requires the exploration of a multi-variable space due to the many components in the final product. Finding the best formulation for a new application, or fine-tuning an existing formulation to meet various customer needs, requires extensive sample preparation and testing. New high-throughput technologies in sample analysis at small volumes are needed. A critical measurement in these industries is the viscosity, or ideally, the rheology of the polymer solutions of interest. Our goal is the development of a multi-sample rheometer for polymer formulations. Towards that goal we have developed a device that simultaneously measures the viscosity of multiple (presently four) samples in a Couette (cup and bob) cell configuration. Each cell contains a bob with an embedded permanent magnet that is oscillated via a uniform oscillating magnetic field in a square, 2-axis Helmholtz coil. The angular displacement of the bob is recorded via a CCD camera. Image analysis is used to determine the amplitude and phase difference of the bob with respect to that of the current applied to the Helmholtz coil. Results from model Newtonian samples spanning three decades in viscosity will be presented.

Wednesday 6:00 Reflections/Waterfront PO64

Rheological properties of bread dough: Application of the Cox-Merz and Laun rules

Richard J. Love[1], Yacine Hemar[1], Robert McKibbin[2], and Marco P. Morgenstern[3]
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Bread dough is a material with a complex rheological behaviour. It is valuable for manufacturers of dough-based food products and process equipment designers to have access to models which describe how bread dough deforms during processing, for example during dough sheeting. In order to apply these models the bread dough's rheological properties must be characterised. This requires time-consuming measurements performed by skilled operators using expensive equipment, which could prevent the application of sophisticated models to plant operation, where a quick result is required.

In this work the rheological behaviour of bread dough was characterised using dynamic and steady shear measurements on three different dough formulations. The dynamic measurements showed that all the doughs behaved as weak gels, while the doughs behaved as pseudoplastic materials in the shear rate range accessed by the rheometer (up to 1 s^{-1}). In order to extend the range of shear rates both the Cox-Merz rule and Laun's rule were used. It was found that the bread dough did not obey these rules well. This was due to the fact that the bread dough properties are changed during the rheological measurements. Nevertheless the properties derived from these measurements were applied to a model of the dough sheeting process and were able to be used to qualitatively distinguish between the behaviours of the three different doughs.

Wednesday 6:00 Reflections/Waterfront PO65

Evaluation of the variability of the WLF constants of extruded soy flour with the extent of cooking

Bharani K. Ashokan and Jozef L. Kokini

Department of Food Science, Rutgers, The State University of New Jersey, New Brunswick, NJ 08901

Williams, Landel and Ferry (WLF) equation is a useful tool in predicting the temperature induced changes in foods and hence knowledge of the WLF constants, which are known to be material properties rather than 'universal values', and their variability is essential. Adequate information on the observed variation of the WLF constants as a function of various processing parameters and storage conditions is not available in food literature.

The objective of the present study is to determine the variation of the WLF constants of extruded soy flour with the extent of cooking of the soy flour.

Roasted, defatted soy flour was cooked at 60°C and extruded at 95° and 145°C and the product was then stored at a water activity of 0.753. The extent of cooking was semi-quantitatively estimated by the preferential solubility of the cooked product in various solvents. WLF constants were determined using time-temperature superposition principles and Ferry's reduction method.

The WLF constants (C_1, C_2), for uncooked soy flour dough have been reported in literature to be (16, 164°C) (Yildiz, 2000). The WLF constants of soy flour extruded at 60°, 95° and 145°C were (44, 204°C), (80, 424°C) and (84, 459°C) respectively at a water activity of 0.753. The variation of the constants was correlated with the extent of cooking that was determined semi-quantitatively.

The WLF constants for extruded soy flour were found to be different from the universal values reported for synthetic polymers and show differences across cooking temperatures. The present study allows a quantitative determination of the effect of cooking on the WLF constants of extruded soy flour and will lead to a better understanding of the variability of the WLF constants in food polymers.

Wednesday 6:00 Reflections/Waterfront PO66

Interfacial rheology system for a commercial rheometer

Eric F. Brown

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Interfacial Rheology is the study of the deformation and flow of thin films at a liquid-gas or liquid-liquid interface when subjected to an imposed force. The film thickness will depend on the film composition, molecular size, and the environmental factors (temperature, pH, ionic strength, etc.). The film properties differ from the properties of the bulk phases on either side of the film. Interfacial rheological properties can be measured in simple shear and compression/dilation. By imposing a stress in an oscillatory mode both viscous and elastic properties can be measured. We have developed a chamber for studying interfacial rheology that can be attached to a commercial rheometer. We present sample data, with an analysis package based on work by Oh and Slattery [J. Coll. Inter. Sci. (1978)].

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Plenary Lectures

8:30 AM Grand Station I/II

Monday, October 13	**Dumbbells, trumbbells, shishkebabs, and pearl necklaces — a gallimaufry of results** R. Byron Bird *Chemical & Biological Engineering, University of Wisconsin*
Tuesday, October 14 *Bingham Lecture*	**The nonlinear response of entangled polymers. Does theory explain all the facts?** Giuseppe Marrucci and G. Ianniruberto *Dipartimento di Ingegneria Chimica, Università Federico II*
Wednesday, October 15	**Development of the science of rheology since its formal inception** Arthur B. Metzner *Chemical Engineering, University of Delaware*

Social Program

Sunday, October 12	**Welcoming Reception**	7:00 PM – 9:00 PM	Reflections/Waterfront (Sheraton)
Monday, October 13	**Awards Reception** *Sponsored by a generous contribution from Thermo Electron Corporation*	7:00 PM – 8:00 PM	Reflections/Waterfront (Sheraton)
	Awards Banquet	8:00 PM	Admiral (Sheraton)
Tuesday, October 14	**Business Meeting**	5:30 PM	Grand Station III (Sheraton)
	Tuesday Night Reception (River Cruise) *Sponsored by a generous contribution from TA Instruments*	7:00 PM	Gateway Clipper Docks
Wednesday, October 15	**Poster Session Refreshments** *Sponsored by a generous contribution from Paar Physica USA*	6:00 PM – 8:00 PM	Reflections/Waterfront (Sheraton)