THE SOCIETY OF RHEOLOGY

78TH ANNUAL MEETING
PROGRAM AND ABSTRACTS

Holiday Inn By The Bay
Portland, Maine
October 8 - 12, 2006

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# Meeting Schedule

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## Session Codes

- **BE** = Blends, Emulsions and Multiphase Flows
- **BS** = Biomaterials, Biological Systems and Self-assembly
- **EP** = Rheology and Structure of Entangled Polymer Systems
- **FM** = Non-Newtonian Fluid Mechanics, Instabilities and Turbulence
- **GP** = General Papers
- **MF** = Microfluidics, Confined Systems and Thin Films
- **MR** = Microrheology
- **PL** = Plenary Lectures
- **PP** = Paper, Pulp and Industrial Processes
- **PS** = Polymer Solution Rheology: Molecular-scale Modeling and Experiments
- **SC** = Suspensions, Colloids and Granular Materials
- **VS** = Viscoelasticity of Solids, Thixotropy and Glasses
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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Vermont PL1

Rheology of biopolymer networks

Paul Janmey

Departments of Physiology, Physics and Bioengineering, University of Pennsylvania, Philadelphia, PA 19104, United States

The macromolecules within biological tissues differ in some respects from those forming most synthetic soft materials. Biopolymers are typically longer, thicker, and stiffer than other macromolecules and often have a large, usually negative, surface charge. The size and stiffness of biopolymers makes it possible to visualize single macromolecules in either dilute solution or within crosslinked or entangled networks. These features have enabled their use to examine fundamental properties of polymer motion. The collective properties of biopolymer gels are also often unusual. Many biopolymer systems exhibit large shear moduli at very low volume fraction, a high degree of strain stiffening at small to moderate strains, and in some cases a large negative normal stress. The strain stiffening of biopolymer gels can be exploited by molecular motors to alter the stiffness of living systems, and non-thermal motions of polymers in such systems create novel rheologic properties. A challenge in the design of synthetic biomimetic materials is to reproduce some of these novel rheological features.

Symposium SC
Suspensions, Colloids and Granular Materials

Organizers: Robert Butera and Jonathan Bender

Monday 9:45 Vermont SC1

Rheological behavior of binary blends of micro- and nanoscale colloidal dispersions

Denis A. Shcherbakov and William B. Russel

Department of Chemical Engineering, Princeton University, Princeton, NJ, United States

Colloidal microspheres suspended at their isoelectric point in an aqueous medium normally flocculate due to attractive van der Waals forces. However, recent experimental findings [V. Tohver et al., Langmuir 17 (26), 8414, 2001] show that adding a small amount of highly charged nanoparticles will stabilize the microspheres within a narrow band of nanoparticle concentrations. As the mixture enters the stable fluid region of its phase diagram, a significant drop in the elastic modulus is observed; upon further addition of the nanoparticles, the modulus recovers as the mixture moves outside the region of stability. To quantify this rheological behavior and explain the balance of forces responsible for the unusual phase behavior, our study uses a multi-step approach combining theory and simulations. A novel sampling technique for discretized lattice Monte Carlo is introduced to simulate efficiently the system with large particle size ratios and short-range electrostatic interactions. The results for a single microsphere agree well with experimental data on nanoparticle adsorption. With two interacting microspheres, contributions from several forces yield the potential of mean force for various nanoparticle concentrations. Effective one-component Monte Carlo simulations then provide radial distributions of suspended microspheres, which are used in a statistical mechanical theory to estimate elastic modulus of the binary blends as the function of nanoparticle concentration.

Monday 10:10 Vermont SC2

Nanoparticles diffuse faster than predicted by the Stokes-Einstein relation in polymer melts

Anish Tuteja1, Michael E. Mackay1, Suresh Narayanan2, Subashini Asokan3, and Michael S. Wong3

1Dept. Chem. Eng. Mat. Sci., Michigan State University, East Lansing, MI, United States; 2Advanced Photon Source, Argonne National Laboratory, Argonne, IL, United States; 3Department of Chemistry, Rice University, Houston, TX, United States

In recent work conducted by some of us we have shown that addition of nanoparticles to polymer melts can cause a large decrease in viscosity. This contradicts the common observation of a viscosity increase on the addition of particles to polymer melts and solutions, as well as Einstein's century old prediction. To understand this phenomenon we measured the diffusion of nanoparticles in polymer matrices and report the first successful direct measurements of translational diffusion coefficients for nanoparticles in entangled polymer matrices using X-ray photon correlation spectroscopy. We find the diffusion coefficients to be up to 100 times larger than that predicted by the Stokes-Einstein relation. Yet, the diffusivity does have an upper bound given by the unentangled Rouse viscosity which the experimental values approach and do not exceed. So, the nanoparticles essentially "feel" some of the entanglements and not all. Since the nanoparticles diffuse so fast we expect that they do not fully participate in the entanglement network perhaps contributing to a constraint release mechanism and the subsequent viscosity reduction.
Graphene-rubber nanocomposites

Bulent Ozbas, Michael J. McAllister, Douglas H. Adamson, Richard A. Register, Ilhan A. Aksay, and Robert K. Prud'homme

Chemical Engineering, Princeton University, Princeton, NJ 08544, United States

We present the effects of incorporation of completely exfoliated graphene nano-platelets on the physical properties of rubber nanocomposites. The functionalized graphene (FG) sheets with aspect ratios on the order of 10000 and with specific surface areas as high as 1500 m²/g are obtained through rapid thermal exfoliation of graphite oxide. Polymer nanocomposites filled with FG offer better or equal physical properties (mechanical, electrical) compared to nanotube, clay and carbon black based composites. The mechanical measurements show that both Young's modulus and tensile strength of natural rubber (NR) increase more than 4 times with only 2 wt % of FG loadings that is comparable to NR composites filled with 20 wt % CB. In addition, the NR-FG composites become electrically conductive at very low filler loadings. The effect of processing methods (melt vs. solution) on the resultant quality of the filler dispersion and physical properties will be discussed. The degree of surface functionality of graphene sheets can be controlled during expansion process without employing an additional process. The effect of functional groups on the physical properties and curing of NR will be presented.

Effect of flow history on structure build-up and breakdown of polymer/clay nanocomposite model systems

Christophe Mobuchon, Pierre J. Carreau, and Marie-Claude Heuzey

Center for Applied Research on Polymers and Composites, Montréal, Québec H3C 3A7, Canada

The properties of polymer/clay nanocomposites are closely related to the clay structure induced by processing flows. The development of a rheological model to probe the clay structure and dispersion in a fluid remains a main challenge. Suitable model systems based on polar Newtonian matrix and non-polar Newtonian and elastic matrices (Boger fluids) have been formulated. The non-polar system is based on a polybutene with a suitable organomodified montmorillonite clay (Cloisite 15A, Southern Clay) while the polar system is based on a polyglycol with a natural montmorillonite clay (Cloisite Na⁺, Southern Clay).

The effect of flow history on build-up and breakdown of the clay structure is investigated by means of a combination of linear and non-linear rheometric measurements. These include small amplitude oscillatory shear (SAOS) to study the clay structure build-up at rest, and transient shear flows with sudden changes in shear rates and large amplitude oscillatory shear (LAOS) to characterize the clay structure build-up and breakdown under flow. For LAOS experiments, fast Fourier-transform rheology (FFT) has been applied while parallel superposition of steady shear flows has been used for SAOS experiments.

Shear induced networks have been observed with a peculiar LAOS behavior with large overshoots for the storage and the loss moduli as functions of strain depending on the preshearing history. Furthermore, after cessation of steady pre-shear flow, the elastic and storage moduli reached different plateau values at long times that were pre-shear rate dependent. These results have been interpreted in light of rheo-optics with dichroism and birefringence measurements. Finally, the structural model of Yziquel¹ has been modified to take into account the effect of flow history.

Topological constraints in entangled polymer melts allow sliding of chains along tubes or, equivalently, through slip-links. Hence, a chain will recover the equilibrium monomer density along its contour after a step deformation, as opposed to a covalently cross-linked network. Lin [1] has assumed that this type of chain sliding motions involves several entanglement segments, that the corresponding relaxation strength is 1/4 of the plateau modulus and that the decay toward equilibrium is characterized by a single exponential. Likhtman and McLeish [2] have recently presented a different theoretical analysis of this phenomenon, which they describe as "longitudinal modes". According to Likhtman and McLeish, monomer redistribution along the tube after a deformation relaxes 1/5 of the stress and the process extends between $\tau_e$, the Rouse time of one entanglement segment, and $\tau_R$, the Rouse time of the whole chain. To our knowledge, no clear experimental rheological evidence of the "monomer reequilibration" or "longitudinal modes" has yet been presented in literature.

By analyzing the linear viscoelastic response of very high MW monodisperse polybutadiene samples, we detect, for the first time, the relaxation process corresponding to monomer density reequilibration. A Maxwell-like peak for $G''$ and a corresponding transition for $G'$ are clearly observed at high frequencies when contributions of the Rouse-like modes are subtracted from the experimental curves as a power law with an experimental exponent close to 0.7. The characteristic time of the chain sliding motions is a few multiples of $\tau_e$. The integral area of the corresponding $G''$ peak is about 1/4 of the area of the terminal peak. These observations have interesting implications for models describing monomer density reequilibration.

A general methodology to predict the linear rheology of branched polymers
Evelyne van Ruymbeke¹, Christian Bailly², Roland Keunings³, and Dimitris Vlassopoulos¹

¹I.E.S.L., F.O.R.T.H., Heraklion 71110, Greece; ²POLY, Universite catholique de Louvain, Louvain-la-Neuve, Belgium; ³CESAME, Universite catholique de Louvain, Louvain-la-Neuve, Belgium

We present a general coarse-grained model for predicting the linear viscoelastic properties of branched polymers from the knowledge of their molecular structure and three viscoelastic parameters, i.e. the Rouse time of an entanglement segment, the plateau modulus and the entanglement molecular weight. The model uses the ingredients of the tube-based theories of McLeish and co-workers, and its implementation is based on a time-marching algorithm; this conceptual approach was already successfully applied to linear and star polymers*, and is appropriately modified here to account for more complex branched architectures, within the framework of dynamic tube dilation (using the extended criteria of Graessley). While the fluctuations of the external branches segments are quite well described in literature, the motion of the molecular segments localized between two branching points is still an open question that we study in this work. With proper account of polydispersity and use of macromolecular coordinates for the diffusion of the branching points, successful description of a wide range of rheological data of H, pom-pom, tree-like or comb polymers is obtained. The good quality of predictions gives us confidence about this approach. More notably, we do not need to use ad hoc parameter modifications (in particular the p2 parameter) to get good results. The proposed methodology thus represents a generic approach for predicting the linear rheology of branched polymers.


Hierarchical relaxation Of asymmetric star polymer melts
Qiang Zhou¹ and Ronald G. Larson²

¹Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, United States; ²Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

Dynamics of asymmetric star polymer melts are studied using molecular dynamics simulations of semi-flexible pear-necklace chains. The slow push-off method for fast equilibrating linear polymer melts is adapted to star molecules, which equilibrates arm configurations at all length scales with affordable computation. The contraction factor, the ratio of star molecule's radius of gyration to that of a linear one with equal total molecular weight, agrees excellently with the Zimm-Stockmayer calculation. The relaxation of a star molecule in a melt is interpreted using the hierarchical relaxation conjecture, i.e., that the short arm first retracts to the branch point; then the backbone relaxes effectively as a line polymer chain with an extra drag from the relaxed short arm. The self diffusion coefficient of star molecules is thereby estimated from the effective drag of the linear chain, which is extracted from the monomer diffusion data of the asymmetric stars using tube theory. An exponential dependence of self diffusion coefficient on the short arm length is found when the short arm has a larger molecular weight than the entangled molecular weight. Interestingly, our result shows a slightly stronger dependence than that was found in experiments.

Symposium BS
Biomaterials, Biological Systems and Self-assembly
Organizers: Srini Raghavan and Surita Bhatia

Macromolecular assembly based on inclusion associations between beta-cyclodextrin and adamantyl grafts
Xuhong Guo¹, Li Li¹, Lin Fu¹, Robert K. Prud'homme¹, Bruce L. May², and Stephen F. Lincoln²

¹Chemical Engineering, Princeton University, Princeton, NJ 08544, United States; ²Chemistry, University of Adelaide, Adelaide, Australia

Due to the strong inclusion association between adamantyl (AD) and beta-cyclodextrin (beta-CD) groups, macromolecular networks are constructed by mixing AD modified poly(acrylic acid) (ADPAA) and beta-CD modified poly(acrylic acid) (beta-CDPAA). The inclusion associations between AD and beta-CD groups are investigated by using rheological method. The maximum viscosity appears at the 1:1 molar ratio of AD to beta-CD groups which means their inclusion associations are binary. The free beta-CD can compete with grafted beta-CD groups and thus destroy the network due to the stronger binding between free beta-CD and AD groups. The viscosity of the polymer networks decreases with increasing temperature. A phase transition appears between 25 and 40 °C. At the temperature region of 10 to 25 °C, the storage modulus and the loss modulus obey time-temperature superposition and master curves can be obtained. The temperature shift factors obey a simple Arrhenius relationship.
Contrasting effects of temperature on the rheology of normal and reverse wormlike micelles
Shih-Huang Tung, Yi-En Huang, and Srinivasa R. Raghavan
Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States

Wormlike micelles are flexible, polymer-like chains formed by the self-assembly of amphiphilic molecules either in water ("normal" worms) or in oil ("reverse" worms). These two classes of micelles exhibit analogous rheological properties (e.g., both can show Maxwell fluidlike behavior). Here, we report a hitherto unexplored difference between these two systems concerning the effect of temperature on their dynamic rheological properties. For normal worms, the plateau modulus remains constant as the sample is heated while the relaxation time exponentially decreases. For reverse worms, on the other hand, both the plateau modulus and the relaxation time decrease exponentially upon heating. In turn, the zero-shear viscosity of reverse worms decreases more rapidly with temperature than for normal worms. The results suggest that both the length and the number density of reverse worms are decreased by temperature, whereas it is only the micellar length that is affected in the case of normal worms.

Effect of pressure and shear on the phase diagram of PLGA-dioxane-water solutions
Sue Ann Lim and Justin J. Cooper-White
Division of Chemical Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

The effect of shear and pressure on the phase separation behaviour of semi-dilute polymer solutions has generated much interest among researchers over the past 20 years. In this paper, the influence of pressure and shear on the phase diagram of PLGA-dioxane and PLGA-dioxane-water mixtures has been investigated. At low temperatures (but above the cloud point temperature of the mixture), the imposition of shear was found to rapidly induce a phase separation in semi-dilute PLGA-dioxane-water solutions. However, for systems with high cloud point temperatures, shear-induced phase remixing was observed when the system temperature was below the cloud point temperature. In the presence of shear, the role of the polymer on determining the phase change behaviour has been found to be strongly correlated with the relaxation time of the solutions (measured using capillary break-up extensional rheometry). For a PLGA-dioxane solution, we found that pressure induces crystallization of the solution such that the crystallization rate increases with increasing PLGA concentration. This phenomena shows a strong correlation with the rate of increase in the solution viscosity that accompanies an increase in pressure for each PLGA concentration. The effect of pressure on the cloud point temperature of PLGA-dioxane-water solutions has also been investigated. For this three component system, it was found that pressures of ~ 200 bar (for a 87/13(v/v) 8%(w/v) PLGA/dioxane/water mixture) lead to a 10°C increase in cloud point temperature.

Effect of solvents on the dynamics of collagen solutions and gels
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Solvents affect the dynamic behavior of proteins [1]. The dynamics of structural proteins in mixed solvent systems reveals the role of chemical environment in mechanical properties of tissues. Using water-soluble collagen samples, in the dilute regime, one can build a system where the protein rods display rather fast dynamics. We use Diffusing Wave Spectroscopy (DWS) to analyze the dynamic behavior of collagen solutions and gels in the wide frequency range. This technique allows for probing the solvent effects on both, fast and slow dynamics of protein solutions. For more concentrated systems, the inter-chain interactions become more important; in this regime, the system becomes non-ergodic. We use camera-based multi-speckle detection technique that may capture very slow dynamic processes. In this case, the dynamics is heterogeneous both
in time and space; we use time resolved correlation technique (TRC) to analyze the slow dynamics associated with sudden structural rearrangements in multi-chain systems. We calculate the statistics of sudden rearrangement events using TRC methodology [2]. Thus, the combination of several approaches for the dilute and concentrated regimes allows studying the effect of solvents on dynamic behavior of collagen solutions and gels.


Symposium FM
Non-Newtonian Fluid Mechanics, Instabilities and Turbulence
Organizers: Lance Collins and R. Sureshkumar

Monday  9:45     Rhode Island
A study on the rheology effects in viscoelastic turbulent channel flows based on DNS
Kostas D. Housiadas\(^1\) and Antony N. Beris\(^2\)
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We present our most recent Direct Numerical Simulations (DNS) results on viscoelastic channel flow using spectral approximations along the spatial directions. A variety of constitutive models have been used in order to study the effect of both the constitutive model and the rheological parameters of the polymer: (a) the Finite-Elasticity Non-Linear Elastic Dumbbell model with the Peterlin approximation (FENE-P) which is widely used to describe the dynamics of dilute polymer solutions, (b) the Giesekus model which takes into account polymer chain interactions and is preferable for semi-dilute polymer solutions and (c) a new combinatorial constitutive model that has both the features of the FENE-P and the Giesekus model (called as FENE-P/Giesekus). In particular, and among the others features, the FENE-P/Giesekus model admits finite extension of the polymer molecules as well as stress anisotropy due to the chain interactions (the predictions of the new model under simple shear, steady elongation and transient elongation are first shown). The simulations for viscoelastic turbulent channel flow showed that the maximum extensional viscosity exhibited by the modeled system and the friction Weissenberg number are considered as the dominant factors determining the levels of drag reduction. In addition, it appears that the apparent shear viscosity and two extensional viscosities, which are also presented, can be correlated with the achieved drag reduction. Statistics of the three invariants of the conformation tensor are also presented and connected with the polymer behavior in the flow. Of particular interest is an attempt to correlate the drag reduction to the model characteristics and its parameter values and this is offered here in connection to results based on the Reynolds and conformation tensor budget (averaged) equations.

Monday  10:10     Rhode Island
A RANS model for turbulent drag reduction by polymer injection and comparison to DNS
Eric S. Shaqfeh\(^1\), Gianluca Iaccarino\(^2\), and Mansoo Shin\(^3\)
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Polymers injected in a turbulent boundary layer are known to reduce the friction drag by as much as 70%. The complex interaction between polymer chains and turbulent structure has been investigated in the past decade using Direct Numerical Simulations (DNS). To investigate the feasibility of using polymer injection to reduce the friction drag on ships and submarines, an engineering physics-based model has been developed. The starting point is an accurate Reynolds-Averaged Navier-Stokes eddy viscosity closure for Newtonian fluid, the v2-f model [Durbin 1995]. The proposed model consists of two parts, the model for the polymer stresses and the closure for the turbulent scalar transport. The polymer stresses are defined in terms of the conformation tensor equations and, in a Reynolds average sense, contain unclosed terms that correlate the turbulent fluctuations to the non-Newtonian stresses. In order to simplify the model, only the polymer elongation is considered, in the assumption that the chains are aligned with the mean strain direction. This allows to consider only one transport equation for the trace of the conformation tensor. The second part of the model, involves the closure of the turbulence equations. Here, a new equilibrium between turbulence production, dissipation and visco-elastic stretching is invoked and this leads to a modification of the pressure-strain term. We shall show comparisons of our RANS model to DNS of channel and boundary layer drag reduction.
Recent developments in numerical simulation have allowed us to obtain accurate and stable Direct Numerical Simulations (DNS) of highly drag reduced (more than 60%) turbulent channel flows of dilute polymer solutions [1]. Various constitutive models have been used: (a) the Finite- Elasticity Non-Linear Elastic Dumbbell model with the Peterlin approximation (FENE-P), which is widely used to describe the dynamics of dilute polymer solutions, and (b) the Giesekus model which takes into account polymer chain interactions and is preferable for semi-dilute polymer solutions. Here, we report on analysis of coherent structures based on that information obtained using a Karhunen-Loeve (K-L) (also called Proper Orthogonal Decomposition (POD)) analysis of the data. Preliminary (static) results at low to moderate drag reduction values have demonstrated a dramatic decrease in the K-L dimension of the flow (by an order of magnitude) as viscoelasticity increases versus the Newtonian case [2]. This work extends that analysis to coherent structure dynamics by studying the time evolution of the projection coefficients of the velocity data against the most significant of the eigenmodes obtained via K-L analysis. Various statistical analyses have been performed on the time-series of projection coefficients, leading to information on the auto-correlations and cross-correlations in the eigenmode coefficients, as well as various characteristic time scales. The results confirm previous predictions of a substantial increase in characteristic time scales imparted by viscoelasticity. An attempt is made to correlate those changes to the underlying structure and the various flow and model parameters of the problem.


We present low-dimensional models for analysis of exact coherent structures in shear flows of viscoelastic liquids aimed at helping interpret experiments and direct numerical simulations of turbulent drag reduction by polymers. These models are developed by systematically investigating the effect of low levels of elasticity on models of exact coherent states in shear flows. It has been recently proposed that the exact coherent structures in shear flows are maintained by a self-sustaining cycle consisting of streamwise rolls that redistribute the mean shear into spanwise streaks. A Kelvin-Helmholtz instability of the spanwise streaky flow then results in the regeneration of the streamwise rolls via nonlinear interactions [F. Waleffe, *Phys. Fluids*, 9, 83 (1997)]. Our 9 dimensional model enables the identification of the part of the cycle that is interrupted or enhanced by the presence of elasticity. We also analyze the ability of low-dimensional models to reproduce qualitatively the Reynolds stresses of higher order models and of DNS of wall-bounded turbulence. We also explore the effect of fluid rheology on the flow kinematics.

Nonlinear traveling waves that are precursors to laminar-turbulent transition and capture the main structures of the turbulent buffer layer have recently been found to exist in all the canonical parallel flow geometries. We present a study of the effect of polymer additives on the dynamical behavior of these "exact coherent states" (ECS) in the plane Poiseuille geometry using direct numerical simulation, focusing on Reynolds numbers slightly above transition. In experiments with a given fluid, Reynolds and Weissenberg numbers (Wi) are linearly related. In this situation, we study the dynamical behavior (i.e. birth, evolution and death) of viscoelastic ECS along some experimental paths (Ei = Wi/Re = const), which represent different flow behaviors as Re (and Wi) increases. These results are then compared with our previous static approach (i.e. in a traveling wave frame), testing the proposed scenario about many key aspects of the turbulent drag reduction: delay in transition to turbulence; onset of drag reduction, diameter and concentration effect, and some observations regarding the nature of maximum drag reduction regime.
Simulations of particle suspensions in viscoelastic fluids
Ahmad Malidi and Oliver G. Harlen
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In many polymer processing applications filler particles such as glass beads are added to the polymer matrix. To study the rheology of such multiphase systems we perform direct simulations of the motion of the suspended particles when subjected to an external linear flow, such as simple shear or extensional flow. In order to make the computations tractable we solve the flow in a unit cell containing a small number of particles with doubly periodic boundary conditions on a self-replicating lattice to replicate a suspension on an infinite domain. Our simulation method combines the Lagrangian-Eulerian technique of Harlen et al (1995), where the constitutive equation is solved in a Lagrangian frame, with a quotient space representation of the lattice to impose the doubly periodic boundary conditions. An advantage of this formulation is that connectivity of the mesh naturally enforces the correct boundary conditions. In shear flow we show that for tube based constitutive models, such as the pom-pom and RoliePoly equations, changes in the rheology due to the addition of filler particles can be accounted for by a simple shifting of the strain-rate and shear stress. However, this does not hold for dumbbell models such as the Oldroyd B and FENE models. We will also compare our simulations results with rheological measurements on suspensions of glass spheres in polystyrene melts. Finally we hope to show results for planar extensional flow.

Motion of a bead through a yield stress and/or thixotropic fluid
Hervé Tabuteau\textsuperscript{1}, Philippe Coussot\textsuperscript{2}, and John de Bruyn\textsuperscript{3}
\textsuperscript{1}Physics and Astronomy, University of Western Ontario, London, Canada; \textsuperscript{2}LMSGC, LCPC-CNRS, Champs, France; \textsuperscript{3}Physics and Astronomy, University of Western Ontario, London, Ontario, Canada

When embedded in a viscoplastic fluid such as a concentrated suspension, a foam or a gel, an object cannot move steadily unless submitted to a force larger than a critical one. We have studied the motion of spheres falling through yield-stress Carbopol gels which exhibit negligible thixotropy. We measured the velocity of the falling sphere as a function of time and sphere density. Three regimes of motion were observed. Spheres of high enough density reached a constant terminal velocity, as in Newtonian fluids. Below a critical density, the sphere came to a complete stop, while in an intermediate regime, the sphere continued to move but with a velocity which steadily decreased with time. Reproducible results were obtained when the experimental fluids were carefully prepared and homogenized. We have also carefully characterized the rheological behavior of the fluids. The flow regimes observed for the falling sphere are analogous to those observed in creep tests for different applied stress levels. The yielding criterion and the drag force on the sphere obtained from our data are in excellent agreement with the longstanding but previously unconfirmed theoretical predictions of Beris (1985) and Beaulne and Mitsoulis (1997). We also carried out experiments with a thixotropic yield stress fluid, i.e. a laponite suspension. In that case the minimum velocity that can be reached (for the critical force) is larger than zero. A further analysis of the data shows that for low velocities the object penetration involves the liquefaction of an extremely thin layer of fluid around the particle surface while the rest of material remains in its solid regime and is mainly deformed elastically.

Sedimentation of two vertical spheres in a xanthan solution
Ronald J. Phillips\textsuperscript{1}, Laurence Talini\textsuperscript{2}, and Emilie Verneuil\textsuperscript{2}
\textsuperscript{1}Chemical Engineering and Materials Science, University of California at Davis, Davis, CA 95616, United States; \textsuperscript{2}Laboratoire FAST, Universite Paris-Sud, Orsay, France

Particle interactions in non-Newtonian fluids differ qualitatively from what is observed in Newtonian fluids, even at very low Reynolds numbers. We have investigated the sedimentation of two identical spheres in a solution consisting of xanthan in a solvent of glycerol and water. When the spheres are aligned vertically, they move together rapidly as they fall, ultimately forming a vertical doublet. By using particle-image velocimetry (PIV), we have measured the velocity field in the region around the spheres, including the "negative wake" above the upper sphere and, in some cases, between the two spheres. In addition, we have performed numerical calculations for the axisymmetric two-sphere problem, using a spectral method in bipolar coordinates. Results from the experiments and calculations will be presented and compared.
Suspensions of particles in liquids are a class of materials relevant in a variety of applications. A variegate spectrum of rheological properties is observed depending on concentration of particles, their mechanical properties, shape, and size, and on the rheology of the suspending liquid. In this work we consider a suspension of buoyancy free, inertialless, rigid, nonBrownian spherical inclusions in viscoelastic liquids. Several rheological predictions are analytically derived through a perturbative approach with the Deborah number, De, as the perturbation parameter. These predictions are confirmed by 3D numerical simulations, which also describe situations at higher De-values. Good agreement is found with a variety of experimental data found in the literature.

**Monday 3:10 Vermont**

**Rheology of a dilute suspension of spheres in a viscoelastic liquid**

Pier Luca Maffettone	extsuperscript{1}, Gaetano D'Avino	extsuperscript{1}, and Francesco Greco	extsuperscript{2}

	extsuperscript{1}Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, Naples I-80125, Italy; \textsuperscript{2}Institute of Composite and BioMedical Materials, CNR, Naples I-80125, Italy

Suspensions of particles in liquids are a class of materials relevant in a variety of applications. A variegate spectrum of rheological properties is observed depending on concentration of particles, their mechanical properties, shape, and size, and on the rheology of the suspending liquid. In this work we consider a suspension of buoyancy free, inertialless, rigid, nonBrownian spherical inclusions in viscoelastic liquids. Several rheological predictions are analytically derived through a perturbative approach with the Deborah number, De, as the perturbation parameter. These predictions are confirmed by 3D numerical simulations, which also describe situations at higher De-values. Good agreement is found with a variety of experimental data found in the literature.

**Monday 3:35 Vermont**

**A fundamental study on the structure of laponite-PEO dispersions using rheology, birefringence and SAXS**

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We present rheology, birefringence and small x-ray scattering (SAXS) on polymer clay dispersions. Our ultimate goal is to determine the structural changes underlying recently observed re-entrant rheological behavior in these systems, and to understand the effect of added polymer on the phase behavior of clay systems. Our model systems consist of the synthetic clay laponite with added poly(ethylene oxide) (PEO). It is well known that laponite forms an isotropic phase at low concentrations (< 3 wt%), while a transition to a nematic phase occurs at higher loadings. Evidence of a rheological transition, similar to re-entrant behavior, with the addition of low molecular weight PEO to clay concentrations up to 3 wt% is observed. Measurements of the structural changes during this transition by birefringence and SAXS are presented. SAXS studies show the structure of the dispersions with the addition of low and high molecular weight. In addition, we show that the isotropic to nematic transition at clay concentrations greater than 3 wt% is effected by the addition of polymer as evidenced by birefringence.

**Monday 4:25 Vermont**

**The bulk viscosity of suspensions**

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The bulk viscosity of a pure compressible fluid is defined as the constant of proportionality relating the difference between the mechanical and thermodynamic pressures to the rate of expansion. Rigid particles suspended in an expanding fluid cause a disturbance flow that contributes to the total mechanical pressure in the system, thereby changing the effective bulk viscosity. For a suspension of particles the bulk viscosity relates the deviation of the trace of the macroscopic or averaged stress from its equilibrium value to the average rate of expansion. The equilibrium macroscopic stress is the sum of the fluid pressure and the osmotic pressure of the suspended particles. We derive expressions to compute the effective bulk viscosity for all concentrations and all expansion rates for a system of rigid particles suspended in a uniformly expanding fluid. To leading order in volume fraction (\(\phi\)) it is shown that the particles contribute \(4/3\eta\phi\) to the effective bulk viscosity, where \(\eta\) is the shear viscosity of the fluid. At higher concentrations, the expansion flow drives the suspension microstructure out of equilibrium and is resisted by the thermal motion of the particles. The contribution to bulk viscosity is determined to second order in volume fraction of particles in both the linear-response regime (small Peclet numbers) and for all compression rates (all Peclet numbers). A "compression thickening" of the suspension is observed at large rates of compression.

In most applications of suspensions, both the fluid and the particles are incompressible, implying that bulk viscosity effects are not important. However, when viewed macroscopically as a phase both the fluid and particle phases are compressible as the particles may come closer together or move further apart and thus bulk viscosity effects may be important for the modeling of suspension behavior.

**Monday 4:50 Vermont**

**Multiscale modeling of electro- and magnetorheological suspensions**

David Kittipoomwong	extsuperscript{1}, Daniel Klingenberg	extsuperscript{1}, Yevgeny Yurkovetsky	extsuperscript{2}, and Jeff Morris	extsuperscript{2}

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Application of an electric or magnetic field to suspensions of polarizable or magnetizable particles, respectively, produces an increase of the apparent viscosity of the suspensions in shear flow. The viscosity increase is rapid, occurring over 1-100 milliseconds. For large applied field strengths, this initial, rapid transient response is often followed by a much slower transient increase in the apparent suspension viscosity. The slow transient response has been associated with the field-induced formation of lamellar structures. A two-fluid continuum model has been employed to investigate the formation of the lamellar structures in these materials. In this model, particle migration is related to the particle contribution to the normal stresses induced by the applied field and by the shear flow. Using naive approximations for these stresses, the model successfully predicts the formation of lamellar structures, and presumably the onset of a slow transient rheological response, for field strengths above a "critical" value. However, the naive approximations result in several other predictions that do not agree with experimental observations.
The dynamics of rodlike particles under sedimentation and induced-charge electrophoresis
David Saintillan, Eric S. Shaqfeh, and Eric Darve
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It is a well-known phenomenon that sedimenting suspensions of rodlike particles undergo a concentration instability resulting in the formation of dense particle clusters. In this work, we discuss the effects of stratification and of an external electric field on this instability.

In stratified suspensions, we show using a linear stability analysis and large-scale simulations that the vertical density gradient stabilizes long-wavelength fluctuations, resulting in a wavenumber selection at a finite wavelength. In initially well-mixed suspensions, the evolution of the wavenumber of the instability can therefore be explained as a consequence of the formation of density gradients in the bulk of the suspensions.

When an external electric field is applied such as in microfluidic applications, and if the particles are polarizable, induced-charge electrophoresis occurs. We use theory and simulations to study this phenomenon, which is shown to cause the alignment of the particles and to drive a stresslet flow in the vicinity of the particles. While this induced flow can result in additional particle pairings, the strong alignment in the direction of the electric field tends to stabilize the suspension, which is observed to become stable for sufficiently strong fields. Upon stabilization, the average sedimentation velocity of the particles is hindered (rather than enhanced as in the unstable sedimentation), and we present calculations of both the stability boundary in terms of the dimensionless applied field, as well as a theory for the hindered settling function.

Oscillatory shear of suspensions of noncolloidal particles
Jonathan M. Bricker and Jason E. Butler
Department of Chemical Engineering, University of Florida, Gainesville, FL, United States

Noncolloidal suspensions undergoing unsteady shear flow present unique behavior not observed under steady shear conditions. To understand the dynamics of suspensions in unsteady shear flow, the rheological behavior under oscillatory flow conditions was studied using experiments and simulations. Experiments were performed to evaluate the stress as a function of the total strain. The rheology has a strong dependence on the applied field strength, shear rate, particle concentration, and shear history. Results for the normal stress components provide improved information to describe both the onset of lamella formation, as well as the long-time structure. Results for the deviatoric stress components provide information about the conventional field-induced rheology as well as its transient behavior.

PME Stokesian dynamics simulations of dense colloidal suspensions with attractive forces: Microstructure of liquids and gels
Michael D. Bybee and Jonathan L. Higdon
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PME Stokesian dynamics simulations are presented for dense suspensions of colloidal particles forming liquid phases or gels. These phases form under the action of short-ranged, weakly attractive particle-particle interactions and Brownian motion. Gel phases have been observed experimentally to exhibit profoundly different microstructures depending upon the origin of the particle-particle attraction. Depletion gels tend to form particle clusters in a quiescent gel state which are broken up upon the imposition of a strong shear flow. By contrast, thermal gels show little particle clustering in the quiescent gel state, but show cluster formation under the action of strong shear. In this study, we investigate the effect of the range and strength of attraction on the gel microstructure and its mechanical and rheological properties. Simulations are conducted for both quiescent and sheared suspensions over a range of volume fraction, Peclet number and attractive force potentials. Balances between short range attractive forces, short range hydrodynamic lubrication forces and stochastic Brownian forces are shown to play an important role in the dynamics of the suspension microstructure.
Our slip-link model is used to make analytic and numeric predictions about the primitive-path-length distribution of a linear, entangled polymer. Such information is useful in predicting the relaxation of stress in star-shaped polymers, and in estimating the relative contribution of chain-length breathing modes in linear chains. Such statistics are also important for examining recent attempts at coarse-graining atomistic simulations. These atomistic simulations have shown an ability to predict entanglement densities, providing one of two essential parameters for tube or slip-link models. However, various competing algorithms exist for making such a prediction. Therefore, it is necessary to examine more-detailed statistics than just the entanglement density, to determine not only the reliability of the algorithm, but also the plausibility of coarse-grained models. Previous work assumed (or approximated) the distribution as Gaussian, in which case the variance can be characterized by a single dimensionless parameter $\nu$. Doi and Kuzuu [J. Polym. Sci., Polym. Lett. Ed. 18, 775 (1980.)] estimated this parameter to be 3/2; numerical results based on the bond fluctuation model were found by Shanbhag and Larson [Phys. Rev. Lett. 94, 076001 (2005)] to be near 3/2, but with a slight dependence on the chain's entanglement number. Recent atomistic simulations by Foteinopoulou, Karayiannis, Mavrantzas and Kroeger [Macromolecules, in press] have shown that the distribution is indeed nearly Gaussian, but that estimates for $\nu$ depend more strongly on entanglement number. We will show that estimates for $\nu$ based on our slip-link model agree with these atomistic simulations. The predictions also have important ramifications about the distribution near zero primitive-path length, strongly affecting predictions about relaxation in branched entangled polymers.

Monday 3:10 Massachusetts EP9

**Probe rheology: A simple method to separate the contributions of constraint release and contour length fluctuations to non-reptation scalings**

Chen-Yang Liu¹, Roland Keunings², and Christian Bailly¹

¹POLY, Université catholique de Louvain, Louvain-la-Neuve, Belgium; ²CESAME, Université catholique de Louvain, Louvain-la-Neuve, Belgium

We systematically investigate the relaxation dynamics of a small fraction (10%) of short entangled probe chains in a high MW matrix. In this way we create a model environment of "permanent entanglements" for the probes where constraint release (CR) mechanisms are suppressed while, in principle, contour length fluctuations (CLF) remain unaffected. Several observations have been made. First, a narrower terminal peak of the probe, with a G'(ω) ∼ ω^{-3/2} high frequency slope, is observed, in agreement with the prediction of the pure reptation. Also, the position of the G' peak shifts to lower frequencies, which means that the longest relaxation time τd of the probes is retarded, as compared with a self-melt of the same MW. The retardation behavior of τd exhibits two regions depending on the number of entanglements (Z). For well-entangled probe chains, the retardation factor is independent of Z and has a value of about 2.5. This agrees with current CR models or the tube dilation picture. At lower Z, the magnitude of the retardation factor increases with decreasing Z, which points to a Z dependence of CR effects and/or an additional influence of chain ends. The Z dependence of the retardation factor leads to a change of the Z scaling for τd of the probes in a high MW matrix. The corresponding exponent is about 3.1, very close to pure reptation. This confirms the overestimation of CLF effects by current tube models recently inferred from observations on the plateau modulus [1]. The MW dependence of CR effects observed from probe rheology is consistent with literature results on tracer and self-chain diffusion. Therefore, CR rather than CLF seems to be the dominant cause of the non-reptation scalings of the longest relaxation time as well as the diffusion coefficient.


Monday 3:35 Massachusetts EP10

** Origins of stress in polymer melts and the implications for single-chain models**

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It is commonly assumed (especially for analytical calculations) that the main contribution to the stress in polymeric liquids is due to the connectivity of the monomers and follows the Kramer's equation. In this talk we examine this assumption using molecular dynamics simulations of many chain systems ranging from the unentangled to the mildly entangled (M/Me~5). We present a new numerical technique for evaluating the stress relaxation modulus and obtained, for the very first time, accurate rheological data from molecular dynamics simulations. We report on significant deviations from the Kramer’s equation for the stress and suggest an alternative expression. We also investigate deviations of the stress relaxation modulus from Gaussian statistics in polymer melts and analyze their consequences for single chain models such as the tube or the slip-links.

Monday 4:25 Massachusetts EP11

**Onset of chain stretch in a highly entangled polyisoprene melt observed using shear measurements and several extensional techniques**

Jens K. Nielsen¹, Ole Hassager¹, and Gareth H. McKinley²

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We measure the viscoelastic properties of a very highly entangled narrow molecular weight polyisoprene melt, with 280 entanglements in steady and transient shear and elongational flows. The storage and loss moduli, obtained through oscillatory shear measurements, are found to be described well by the Milner and McLeish reptational model. The relaxation modulus G(t;\gamma) is measured using stress relaxation after a sudden shearing displacement and we experimentally determine the Rouse time (tR) by observing strain-time separability G(t)=G(t;\gamma)h(\gamma) for t>tR. The transient elongational properties have been measured using three distinct instruments; the SER universal testing platform from Xpansion Instruments, its counterpart the EVF from TA instruments, and a Filament Stretching Rheometer (FSR). The kinematics obtained in each device are sensitive to the aspect ratio of the sample and care must be taken to achieve homogeneous deformation conditions. We find that the initial growth in the tensile stress follows the prediction given by the Doi and Edwards reptational model, at Rouse-time Deborah numbers, DeR, less than unity. The transient uniaxial elongational viscosity follows the linear viscoelastic envelope with very little strain hardening. Consequently the elastic sample ruptures and fails close to the maximum in engineering stress, in agreement with the Consideré criterion at moderate Hencky strains well before steady elongation is reached. At DeR >1 sample rupture is not encountered until 6-7 Hencky strain units, and the tensile stress differences rise above the Doi Edwards prediction, exhibiting strain hardening. The transient elongational viscosity exceeds the linear viscoelastic envelope at Hencky strains greater than unity. We interpret this to be a clear signature of the onset of chain stretching in this very highly entangled polymer for elongational deformation rates faster than the inverse Rouse time.
Shear and elongational behavior in fast flows of monodisperse polymer melts with a wide range of molecular weights

Dietmar Auhl¹, Jorge Ramirez², Alexei E. Likhtman², Tom C. McLeish¹, Pierre Chambon³, and Christine M. Fernyhough³

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Non-linear rheological properties of polymer melts are of high interest for the processing performance of thermoplastics and its prediction using constitutive equations. In the literature many publications deal with the non-linear rheological behavior of polymer solutions. However, in the case of monodisperse polymer melts not much data have been published.

Experimental and theoretical work on the non-linear shear as well as uniaxial elongational flow behavior is presented. The samples investigated are linear monodisperse polyisoprene and polystyrene melts. The molecular weights of the samples studied differ in about two orders of magnitude resulting in a large range for the number of entanglements. Non-linear viscoelastic properties in shear have been determined at different temperatures from constant strain-rate tests, followed by reverse flow and relaxation tests. Stressing experiments in uniaxial elongation have been used to investigate the non-linear behavior in a stronger flow type for comparison.

The results on the non-linear viscoelastic behaviour are compared to the predictions of molecular models such as a tube CCR model and a slippings model, which are capable of describing fast flows of entangled polymers. Model parameters have been determined from the linear viscoelastic behavior using master curves of dynamic-mechanical data. Characteristic features of the flow curves, e.g. the stress overshoot as well as strain hardening, are discussed as a function of average molecular weight, temperature, and strain rate, respectively.

Rheological behavior of polymer melts in equibiaxial elongational flow using a modified lubricated squeezing flow technique

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Despite its technological significance, the rheological behavior of polymer melts in equibiaxial elongational flow is largely unexplored and, consequently, is inadequately understood. The simple reason for this is that methods for generating equibiaxial elongational deformations are either very complicated or not reliable. The most widely accepted method for generating rheologically controlled, equibiaxial elongational flow is the rotating clamp method, or MultiAxiale Dehnung (MAD), developed by Meissner. However, the extremely complicated nature of the MAD rheometer has resulted in a relatively limited set of experimental data. A promising method that has been used with some success is known as Lubricated Squeezing Flow (LSF), where a polymer melt is squeezed between lubricated surfaces. Unfortunately, uncontrolled lubricant thinning limits the LSF technique to rather modest strain levels. Here we report the first direct comparisons of data obtained with the LSF and MAD techniques. These comparisons were made using the same polystyrene and low-density polyethylene melts used by Meissner. We find that the data obtained using LSF deviate from the MAD data at Hencky strains of less than one, and display behavior that could easily be mistaken for strain hardening. The main objective of this study is the development of a modified LSF technique that involves the continuous injection of lubricant through porous metal plates. Design and fabrication issues of the modified technique are briefly discussed. We also report the first measurements of transient equibiaxial elongational viscosity obtained using the modified LSF technique and make comparisons with data from the MAD rheometer.

Comparison of the elongational behavior of various polyolefins in uniaxial and biaxial flows

Florian J. Stadler¹, Akihiro Nishioka², Jens Stange³, and Helmut Münstedt¹

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For processing operations in which elongational flows play a dominant role it was found that the uniformity of deformation is improved by the presence of strain hardening [1] usually measured in uniaxial elongation. Many of the processing operations such as foaming, film blowing, and blow molding are dominated by biaxial deformations and, therefore, the question arises how strain hardening in uniaxial and biaxial deformation compare. In the literature some few measurements can be found which qualitatively demonstrate the concurrent existence of strain hardening in uniaxial and biaxial elongation [2,3]. This paper intends to give a more detailed insight into these relationships.

For this purpose three polyethylene and two polypropylene melts of different molecular architecture were characterized in uniaxial and biaxial elongation. A linear polypropylene and polyethylene, a highly branched LDPE, and an electron beam irradiated PP were chosen. For the uniaxial elongation the Münstedt Tensile Rheometer (MTR) and the ARES-EVF were used, while the lubricated flow method was applied for biaxial elongation.

It was found that the strain hardening in uniaxial elongation is similar to that in biaxial elongation, but that it is more pronounced for the uniaxial deformation. The dependence of strain hardening on strain rate is qualitatively the same in both modes but it is different for the various samples. In the case of the long-chain branched LDPE and PP the strain hardening is approximately independent of the elongational rate whereas for the HDPE it becomes smaller with increasing rate.
The data was evaluated with the MSF-model and it was found that the uniaxial and biaxial data can be modeled to some extent using the same parameters.


Monday 6:05 Massachusetts

**Elongational viscosity of multiarm (Pom-Pom) polystyrene**

Jens K. Nielsen, H. K. Rasmussen, K. Almdal, and Ole Hassager

*Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark*

Two branched narrow molar mass distribution polystyrene melts have been synthesized: A multiarm A_nAA_n Pom-Pom polystyrene and AA_n asymmetric star polystyrene where n indicates the number of arms. The Pom-Pom and asymmetric star have molar masses 260 kg/mol and 255 kg/mol, respectively. The Pom-Pom was estimated to have 2.5 arms on average, while the estimate is 3.3 for the asymmetric star. The molar mass of each arm is about 27 kg/mol. The melts were characterized in the linear viscoelastic regime and in non-linear elongational rheometry. The transient elongational viscosity for the Pom-Pom molecule was found to be separable in time and strain for elongation rates larger than the inverse reptation time. Up to a Hencky strain of 2.7, the corresponding strain tensor component is closely approximated by a model that assumes the arms to be fully relaxed while the backbone is part of an unrelaxed entanglement network model. At Hencky strain above 2.7 a saturation of stress occurs that we interpret as withdrawal of the arms into the backbone tube. The observed strain associated with arm withdrawal is significantly larger than that predicted from an equilibrium force balance on the branch points while it corresponds well with an estimate of the maximum stretchability of the backbone. Time-strain separability was not observed for the 'Asymmetric star' molecule at the elongation rates investigated. The transient elongational viscosity for the 'Pom-Pom' molecule went through a reproducible maximum in the viscosity at the highest elongational rate.

**Symposium BS**

**Biomaterials, Biological Systems and Self-assembly**

Organizers: Srinivasa Raghavan and Surita Bhatia

Monday 1:55 Connecticut

**Sequence-dependent kinetics of β-hairpin oligopeptide hydrogels**

Travis H. Larsen and Eric M. Furst

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The gelation kinetics of self-assembling hydrogels consisting of β-hairpin oligopeptides are investigated using microrheology and far-UV circular dichroism (CD) spectroscopy. The 20-residue peptides are composed of an alternating sequence of high β-sheet propensity valine and lysine residues flanking a central tetrapeptide designed to adopt a type-II' turn structure. Electrostatic interactions between residue side chains can be manipulated to initiate folding and assembly, leading to hydrogel formation. For example, under acidic conditions, the lysine side chains are protonated, which prevents peptide folding and self-assembly. Intramolecular folding can be triggered by either screening some of the lysine-based charge with salt at physiological pH, or by neutralizing the lysine point charges by increasing the pH of low ionic strength solutions. The transient elongational viscosity for the Pom-Pom molecule was found to be separable in time and strain for elongation rates larger than the inverse reptation time. Up to a Hencky strain of 2.7, the corresponding strain tensor component is closely approximated by a model that assumes the arms to be fully relaxed while the backbone is part of an unrelaxed entanglement network model. At Hencky strain above 2.7 a saturation of stress occurs that we interpret as withdrawal of the arms into the backbone tube. The observed strain associated with arm withdrawal is significantly larger than that predicted from an equilibrium force balance on the branch points while it corresponds well with an estimate of the maximum stretchability of the backbone. Time-strain separability was not observed for the 'Asymmetric star' molecule at the elongation rates investigated. The transient elongational viscosity for the 'Pom-Pom' molecule went through a reproducible maximum in the viscosity at the highest elongational rate.

Monday 2:20 Connecticut

**Correlation between gel structural properties and macromolecule diffusion in self assembling peptide hydrogels**

Monica C. Branco, Norman J. Wagner, Darrin J. Pochan, and Joel P. Schneider

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Self assembling peptides form hydrogels with potential use in drug delivery and tissue engineering applications. We present a family of de-novo peptide designs that link the intramolecular folding of amphiphilic β-hairpin peptides to their propensity to self assemble, affording hydrogel materials. These peptides adopt a random coil conformation in aqueous solutions and are freely soluble. However, when subjected to a stimulus, such as a change in pH, ionic strength, or temperature, the peptides fold into a β-hairpin, and subsequently, self-assemble to form a structurally rigid hydrogel stabilized by non-covalent crosslinks. The gelation rate and mechanical rigidity of the hydrogels have been found to be directly influenced by the peptide concentration and the temperature at which gelation is triggered. As a result, these physico-chemical changes also affect the porous morphology within the hydrogel system to assess the feasibility of using these gels for macromolecule delivery. Here, we investigated the influence of the peptide network in the gels formed at different temperatures and concentrations on the mobility of large macromolecules.
molecules in the system. Rheology reveals that increasing the peptide concentration and the temperature at which the hydrogel is formed results in materials with higher rigidity. Using confocal microscopy combined with fluorescence recovery after photobleaching to measure the diffusion coefficients of FITC-dextran macromolecules in the hydrogel, it was observed that the mobility of the probes, in particular those of larger in size, was greatly influenced by the rigidity of the gel.

Monday 2:45 Connecticut BS8

**Basement membrane protein gels: Architecture and gelation kinetics**
Helena I. Hadisaputra¹, Yoosup Park¹, Andrea J. O'Connor², and Justin J. Cooper-White¹
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Matrigel (BD Biosciences) is a frequently used basement membrane extract for in vitro culture of cells. Although Matrigel (tm) is proven to be an ideal environment for cell growth and differentiation, the fact that it is the extracellular matrix extracted from mouse Engelbreth-Holm-Swarm (EHS) tumors prohibits its in vivo use in humans. Many groups are therefore seeking an alternative support matrix, with similar structural, rheological and biochemical properties as Matrigel (tm), based on other biological or synthetic polymers or a combination thereof. It is the aim of this work to provide the required dynamic rheological data and architecture of basement membrane protein gels composed of Matrigel (tm), laminin-1 and type IV collagen that may be used as references when designing alternative matrices. In this work, cryo-SEM is employed to investigate the unique three dimensional structures of hydrogels made from Matrigel (tm) and its major protein components, laminin-1 and type IV. The dynamic rheological properties of Matrigel (tm) and laminin-1 were characterized as a function of protein concentration, temperature and heating rate (these gels traditionally gel with increasing temperature). The results show that increasing the temperature of Matrigel (tm) from 4º to 37ºC results in an increase in the shear modulus of 100kPa. At the same gelation temperature of 37ºC, Matrigel (tm) has a higher storage modulus compared to laminin-1 alone (30kPa and 4kPa, respectively). Collagen IV (at the concentration available in MatrigelTM) did not gel. Matrigel (tm) also has a lower gelation temperature than laminin-1 (8º and 17ºC, respectively, at 1 rad/s frequency). Given that Matrigel is composed of ~80% laminin-1, these results suggest that laminin-1 alone can form a structurally robust gel but it is the interaction with other structural proteins such as collagen IV and nidogen that allows Matrigel to possess its optimum mechanical properties required by cells.

Monday 3:10 Connecticut BS9

**Rheological fingerprinting of pedal mucus from terrestrial gastropods (snails and slugs) using large amplitude oscillatory shear (LAOS) experiments**
Randy Ewoldt, A E. Hosoi, and Gareth H. McKinley
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Many gastropods, such as snails and slugs, crawl using adhesive locomotion, a technique that allows the organisms to climb walls and walk across ceilings. These animals stick to the crawling surface with an excreted thin layer of a biopolymeric mucin gel, known as pedal mucus, and their acrobatic ability is due in large part to the yield stress character of the slime. The pedal mucus under a crawling snail is subjected to large amplitude periodic simple shear flow, which motivates the characterization of the non-linear properties in large amplitude oscillatory shear (LAOS). The nonlinear material response as a function of imposed stress and frequency can be visualized using Lissajous figures and analyzed quantitatively using Fourier transform rheology in conjunction with an appropriate measure of non-linear elasticity. A Pipkin diagram can represent the full rheological behavior of pedal mucus, and acts as a thorough fingerprint of the material properties.

Monday 3:35 Connecticut BS10

**Forisome: A smart plant protein inside a phloem system**
Steve Warmann¹, Amy Shen¹, and William Pickard²
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With the discovery of the plant protein forisome, a novel, smart non-living, ATP-independent biological material became available to the designer of smart materials for advanced actuating and sensing. Forisomes are unique contractile protein bodies that function as cellular stopcocks in sieve tubes of the Fabaceae. They can block individual sieve elements by undergoing reversible conversions between a low-volume, spindle-shaped, crystallloid conformation and a high volume, spheroidal, disordered conformation; this conversion is accompanied by longitudinal shortening and radial expansion. The in vitro studies show that forisomes (1-3 micron wide and 10-30 micron long) can be repeatedly stimulated to contract and expand anisotropically by shifting either the ambient pH or the ambient calcium ion concentration. Possible applications of forisomes will also be discussed.
Monday Afternoon

Nanoparticle reinforced associative network hydrogels of PLA-PEO-PLA triblock copolymers

Sarvesh K. Agrawal1, Naomi Sanabria-DeLong2, Gregory N. Tew2, and Surita R. Bhatia1

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Hydrogels of poly(lactide)-poly (ethylene glycol)-poly (lactide) have potential applications in drug delivery and tissue engineering. Control over the structure and rheology of the gels is of fundamental importance for the use of this polymer in medical applications. We have performed a complete rheological and structural characterization of these hydrogels using dynamic mechanical rheology, SANS, and USAXS. These polymers form very stiff hydrogels and the structure and properties of these materials can be substantially modified by varying the crystallinity or degree of polymerization (DP) of the hydrophobic PLA block. We have also created reinforced hydrogels with enhanced mechanical properties by addition of laponite nanoparticles. Our recent studies show that the elasticity of the PLA-PEO-PLA hydrogels can be enhanced by orders of magnitude by addition of small amounts of laponite particles to the hydrogels. It is expected that the triblock copolymer micelles adsorb on the surface of the laponite particles to form additional junctions in the hydrogels leading to enhancement in their elasticity. We verify this hypothesis using DLS and SAXS techniques.

Modeling and structure-property relations in tissue engineered collagen scaffolds

Jia Ma, Jennifer Larker, and Jonathan W. Bender

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UV cross-linked collagen provides a robust matrix for the in vitro engineering of cartilage and cardiac tissue. Cells seeded in this matrix remodel their environment, dramatically changing mechanical properties. Most studies of the mechanical properties of cartilage focus on a simple measurement of quasi-static elastic modulus. We show that simple rheological models, such as a non-linear Maxwell-like model, can be used to fit stress-strain and relaxation data. These parameters can then be linked to microstructural features of the collagen matrix, as measured through SEM, AFM, and Confocal microscopy, thereby providing greater insight into the development of mechanically robust tissue.

Viscoelastic properties of a biodegradable, acellular xenogenic scaffold for the bioengineering of vocal fold tissues

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An implantable tissue replacement for the surgical reconstruction of the human vocal fold lamina propria has been developed in our laboratory. A novel proteolytic enzyme-free, detergent-free saline based protocol was employed to decellularize the bovine vocal fold lamina propria into an acellular matrix, resulting in a three-dimensional, biodegradable, acellular scaffold that can be repopulated with fibroblasts for the repair and replacement of pathological host tissue. Viscoelastic shear properties of the scaffold were quantified by a custom-built controlled-strain, linear simple shear rheometer system that is capable of direct empirical measurements of the complex shear modulus of low-modulus biomaterials and soft tissues at frequencies of up to 250Hz. Results showed that the elastic shear modulus, viscous shear modulus and damping ratio of the fibroblast-repopulated scaffold were comparable to those of native human vocal fold tissues, specifically the superficial layer of the lamina propria that is responsible for vocal fold vibration. These findings supported the biomechanical benefits of the scaffold as a xenograft for vocal fold reconstruction and regeneration [Work supported by the National Institutes of Health].

The mechanical behaviour of brain tissue: Large strain response and constitutive modeling

Gerrit W. Peters, Matej Hrapko, Hans A. van Dommelen, and Jac S. Wismans

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The non-linear mechanical behaviour of porcine brain tissue in large shear deformations is determined. An improved method for rotational shear experiments is used, producing an approximately homogeneous strain field and leading to an enhanced accuracy. Results from oscillatory shear experiments with a strain amplitude of 0.01 and frequencies ranging from 0.04 to 16 Hz are given. The immediate loss of structural integrity, due to large deformations, influencing the mechanical behaviour of brain tissue, at the time scale of loading, is investigated. No significant immediate mechanical damage is observed for these shear deformations up to strains of 0.45. Moreover, the material behaviour during complex loading histories (loading-unloading) is investigated. Stress relaxation experiments for strains up to 0.2 and constant strain rate experiments for shear rates from 0.01 to 1 s⁻¹ and strains up to 0.15 are presented. A new differential viscoelastic model is used to describe the mechanical response of brain tissue. The model is formulated in terms of a large strain viscoelastic framework and considers non-linear viscous deformations in combination with non-linear elastic behaviour. This constitutive model is readily applicable in three-dimensional head models in order to predict the mechanical response of the intra-cranial contents due to an impact.
Recently the term "socio-microbiology" has been introduced to describe research on different aspects of bacterial communities [1]. Certain social phenomena like quorum sensing (QS) and 'swarming' in several bacterial species seem to be connected instead of operating separately. For example, swarming is a group behaviour enabling bacteria to spread 'coordinately' and rapidly in a thin film of extracellular material atop solid surfaces [2]. It has been previously suggested that to achieve cell-cell communication in gram-negative bacteria, long chain N-acylhomoserine lactone molecules (AHL) play an important role. Here we investigate their function in swarming in a 'model' bacterium; Rhizobium Etli. Etli colonizes and infects the roots of its host plant Phaseolus vulgaris, the common bean plant. We will show that, besides a possible signaling function, the long chain AHLs also play a direct role in surface movement of the swarmer cells. Surface pressure measurements show that these AHL display significant biosurfactant activity. The complex shape of the swarming colonies suggests that the role of surface-activity in controlling swarming is due to Marangoni effects. Using an analysis presented by Matar and Troian [3], it can be shown that the experimentally observed swimming speed is consistent with the one expected for Marangoni flows for the surface pressures, thickness and bulk viscosities which have been measured. The AHL molecules also affect the flow curve of the extracellular slime in which the bacteria move. Considering these findings, it might be appropriate to re-evaluate the function of AHLs with long acyl-side chains with respect to a direct role affecting the surface tension gradients and the presence of Marangoni effects.


Symposium FM

Non-Newtonian Fluid Mechanics, Instabilities and Turbulence

Organizers: Lance Collins and R. Sureshkumar

Monday 1:55 Rhode Island

The axisymmetric instabilities of electrically-driven viscoelastic jets

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Electrospinning is a novel process that allows the production of nanoscale fibres by using electrostatic force to accelerate a fluid jet. The decisive phase in the process is the region of jet instability, where it is believed that most of the jet thinning occurs. We focus on the onset of axisymmetric instability modes. These instabilities result in the production of beaded nanofibres, which are often seen in practice. We have recently presented a model for the development of the initial stable electrospun jet, where the laws of electrohydrodynamics (momentum equations and Gauss's Law) are fully coupled with viscoelastic polymeric constitutive equations. We now extend this model, and perform a linear stability analysis on the jet. This analysis allows us to identify two distinct unstable axisymmetric instability modes, and to predict the growth rate and critical wavelength of each. By using an energy analysis, the interplay between base state and perturbation for each instability mode has been identified. For low electrical-conductivity fluids, the dominant instability mode is seen to be capillary-driven, whereas for higher conductivity fluids, the instability modes are more complex, and are driven by the interaction of the electric field with the jet. Our stability analysis also reveals that the viscoelasticity of the fluid has a strong influence on the stability characteristics of these axisymmetric modes, affecting the growth rates and critical wavenumbers. Axisymmetric instabilities observed during the electrospinning of polymer solutions with various conductivities (PIB Boger fluid, PEO/water solutions, PS-based solutions) have been captured using high-speed photography. The instability characteristics (wavelength and growth rate) are extracted using image analysis, and are compared with the model predictions.

Monday 2:20 Rhode Island

Pattern formation in viscoelastic Taylor-Couette flow: Ribbons, oscillatory strips, disordered states and diwhirls

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We report spatio-temporal pattern formation in Taylor-Couette flow (i.e. flow between rotating cylinders) of viscoelastic dilute polymer solutions obtained for the first time from first principle dynamical simulations using a parallel, fully spectral time-splitting algorithm. Experimental investigations of pattern formation in viscoelastic TCF have uncovered a variety of intriguing flow transitions including rotating standing waves (RSW), disordered oscillations (DO) and solitary vortex solutions which can be time-dependent (oscillatory strips (OS)) or time-invariant (diwhirls (DW)). However, to date, theoretical investigations have been limited to weakly nonlinear analysis or computation of axisymmetric steady states. This has limited the understanding of the mechanisms of flow-microstructure coupling underlying the pattern formation process which, as shown by experiments, inherently includes creation/destruction of spatial (i.e. axisymmetry vs. non-axisymmetry, periodicity in the direction of the cylinder axis) and temporal (i.e. stationary, time-periodic or disordered) symmetries which can be captured
only by means of a fully 3-dimensional dynamical simulations. In this presentation, we will report, the principal findings of such dynamical explorations and discuss the pattern formation mechanisms. Solution structures with varying spatial and temporal symmetries, such as rotating standing waves, flames, disordered oscillations, and solitary vortex solutions which include diwhirls (stationary and axisymmetric) and oscillatory strips (axisymmetric or non-axisymmetric) are observed, depending on the ratio of fluid relaxation time to the time period of inner cylinder rotation. The flow-microstructure coupling mechanisms underlying the pattern formation process are also discussed.

Monday 2:45 Rhode Island    FM8

3-D instabilities, rheology effects and the influence of the surrounding air on the film blowing process

Kostas D. Housiadas\textsuperscript{1} and John A. Tsamopoulos\textsuperscript{2}

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The well-known process for manufacturing biaxial oriented films of polymer materials, the Film Blowing Process (FBP), is studied. In particular, the stability of the multiple steady state solutions of the governing equations of the process in the thin film limit and under axial symmetry is investigated. This is accomplished by extending the rigorous methodology we developed for axisymmetric annular films with two or three moving unknown interfaces [Housiadas & Tsamopoulos, Phys. Fluids, 1998] to include non-axisymmetric variations. The final partial differential equations, which are valid in the thin film limit, in axial and azimuthal directions and in time are derived. Viscous, inertia, gravity and forces due to the surface tension are also included in the model. Viscoelasticity of the flow is taken into account utilizing the Upper Convected Maxwell (UCM), the Oldroyd-B and the non-linear affine Phan-Thien-Tanner (PTT) constitutive models. Non-isothermal effects are neglected (work with additional constitutive models and non-isothermal conditions is in progress). These highly non-linear differential equations are solved simultaneously at steady state under the assumption of axial symmetry. Next, linear stability analysis is applied examining both axisymmetric and non-axisymmetric perturbations of the base state. The stability analysis revealed that, for all the above constitutive models, the stability regions of the process are significantly shrunk due to non-axisymmetric perturbations. The effect of the air supplied circumferentially to the outer free surface in order to control the location of the freezing line as well as to stabilize the bubble is also studied. This is achieved by extending further the above described procedure and taken into account the flow field of the surrounding air. The preliminary results showed that the air drag affects mostly the lower part of the bubble not allowing for big departures from the vertical position.

Monday 3:10 Rhode Island    FM9

Low Reynolds number unstable flows of complex fluids with pH dependent rheology: Experimental evidence, stability analysis, applications

Teodor I. Burghelea\textsuperscript{1}, Ian A. Frigaard\textsuperscript{1}, James J. Feng\textsuperscript{2}, and Mark Martinez\textsuperscript{3}

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We present an experimental investigation of low Reynolds number horizontal displacement flows of a yield stress fluid with local pH dependent rheology, (Carbopol). Unbalanced free charges near the interface between the two fluids can trigger an acid-base type chemical reaction which results in a local stratification of both the viscosity and the yield stress of the fluid. We show that such local pH dependent fluid rheology may cause an inertia free flow instability. The instability is investigated by means of Laser Induced Fluorescence (LIF) technique and Digital Particle Image Velocimetry (DPIV). Visualization of the chemical reaction front by using pH sensitive dyes allows us to elucidate the mechanism of the flow instability. We also present preliminary results of a linear stability study of the flow. Finally, we discuss a practical application of this instability in efficiently displacing viscous fluids in a horizontal pipe. We demonstrate that the displacement efficiency (defined via the time needed to completely remove the viscous fluid from the pipe walls) can be increased nearly by a factor of two when the local chemical reaction is switched on. This flow instability has both laboratory interest and industrial applications.

Monday 3:35 Rhode Island    FM10

Viscoelastic fluid flows simulations with a generalized log-conformation formulation: A simple and effective approach

Oscar M. Coronado\textsuperscript{1}, Dhruv Arora\textsuperscript{1}, Marek Behr\textsuperscript{2}, and Matteo Pasquali\textsuperscript{1}

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The simulation of complex flows of complex fluids (fluids with inherent micro-macro structure such as paint or blood) poses several numerical challenges, and because of their importance in several industrial applications, considerable effort has been given to the development of robust and stable numerical methods. In this effort, an important contribution to alleviate the long-standing high Weissenberg number problem associated with the viscoelastic fluid flows has been given by the log-conformation formulation [R. Fattal and R.J. Kupferman, Constitutive Laws for the Matrix-Logarithm of the Conformation Tensor, JNNFM, 123 (2004) 281-285]. This formulation guarantees the positive-definiteness of the conformation tensor given by its physical nature, and it is able to capture sharp elastic stress boundary layers; however, the implementation presented in literature thus far requires changing the evolution equation for the conformation tensor into an equation for its logarithm, and are based on loosely coupled solution procedures [M.A. Hulsen, R. Fattal and R. Kupferman, Flow of Viscoelastic Fluids Past a Cylinder at High Weissenberg Number: Stabilized Simulations Using Matrix Logarithms, JNNFM, 127 (2005) 27-39].
In this work, a simpler yet very effective approach to implement the log-conformation formulation in a DEVSS-TG/SUPG code [M. Pasquali and L.E. Scriven, Theoretical Modeling of Microstructured Liquids: a Simple Thermodynamic Approach, JNNFM, 120 (2004) 101-135] for a generalized constitutive model is presented. The governing equations (continuity, conservation of momentum and constitutive equation) are solved in a coupled way by Newton's method. This new formulation is tested in two benchmark problems: Couette flow of Larson-type fluids and flow past a cylinder in a channel of Oldroyd-B fluid. The accuracy of results are compared with the analytical and published results, and the method is found to be highly promising for viscoelastic fluid flow simulations.

Monday 4:25 Rhode Island

Discontinuous Galerkin methods for simulating viscoelastic flow

Shuyu Sun

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Modeling and simulation provide a non-intrusive and effective way to probe the dynamics of viscoelastic fluids. A modeling system of viscoelastic flow mainly involves the equation of momentum conservation together with a constitutive equation, sometimes also coupled with conservation of mass and energy, in addition to boundary and initial conditions for particular geometries such as extruders and mixers. Popular numerical approaches for solving this system include finite difference, finite volume, and finite element methods, though spectral schemes, boundary element methods and cellular automata also have limited applications. Numerical simulations of viscoelastic flow are challenging because the model equation system involves velocity, pressure and extra stress tensor that are strongly coupled across multiple time and spatial scales. In addition, the advection-dominated component and the nonlinear interactions often result in sharp physical quantities, which requires minimal numerical diffusion and oscillation.

DG methods are specialized finite element methods that utilize discontinuous spaces to approximate solutions. Derived from variational principles by integration over local cells, the methods are locally mass conservative by construction. Boundary conditions and interelement continuity are weakly enforced in DG; consequently, DG methods have small numerical diffusion and little oscillation. In addition, they handle rough coefficient problems and capture the discontinuity in the solution well and are flexible for the treatment of full-tensors. In this talk, we formulate a family of primal DG numerical schemes, namely SIPG, OBB-DG, NIPG and IIPG, for viscoelastic flow. Efficient implementation issues are discussed with emphasis on dynamic mesh adaptation strategies. A number of numerical examples are presented to illustrate various features of DG methods for viscoelastic flow systems.

Monday 4:50 Rhode Island

Rheology and fracture (breakup) of liquids

Vladimir M. Entov and Alexey N. Rozhkov

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Breakup or fracture of liquids is a wide-spread phenomenon, important both in everyday life and multifarious industrial processes. In some cases, we are interested in dividing fluid into tiny fragments or drops, in other, the liquid ‘tenacity’, i.e. its ability to resist rupture, is of primary importance. Unlike brittle fracture of solids, fracture of a liquid can not be characterized by a critical value of stress, or strain, but represents a process, sometimes involving several successive stages. This becomes quite obvious in studies of complex fluids, such as water or hydrocarbon liquids thickened by polymers and surfactants. The talk demonstrates a number of examples of experimental studies of breakup of complex fluids. A common feature of all these studies is that at the final stage of breakup ‘necks’ or filaments develop between two adjacent fluid volumes, and rupture occurs via capillary thinning of the filaments. This stage of breakup is studied in much detail both theoretically and experimentally. The thinning may be autonomous, in the sense that it is controlled only by local parameters of the neck, or may be related to global dynamics. Examples of both kinds are shown. Importance of surface tension in all studied scenarios of fluid fracture poses a general question, whether it is feasible to rupture a volume of viscous fluid in the absence of surface tension, and if ‘yes’, what are criteria discriminating the ‘rupturing’ from ‘non-rupturing’ external fields fields? Possible approaches to resolving this issue are discussed.

Monday 5:15 Rhode Island

Numerical simulation of non-dilute suspensions in viscoelastic fluids in an elongational flow

Gaetano D’Avino¹, Pier Luca Maffettone¹, Martien A. Hulsen², and Gerrit W. Peters²

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Stretching of polymer melts is quite common in several industrial processes like thermoforming, fiber spinning and blow molding. Thus, the elongational viscosity of polymers plays a crucial role in predicting the properties of the final products. The presence of an inclusion locally modifies the imposed elongation flow and partially suppresses strain hardening as shown for example by High Impact Polystyrene (HIPS) samples with different dispersed polybutadiene particles. In order to predict the observed features we have developed a two-dimensional numerical model of planar elongational flow accounting for viscoelasticity of the suspending fluid. The particles are treated as rigid disks. The numerical scheme is based on the DEVSS-G/SUPG technique combined with the recently developed log-conformation representation (LCR) to improves numerical stability of the computation of the conformation tensor at high Weissenberg number. The particles are implemented with a rigid ring constraint in a fictitious domain approach using a fixed mesh.
Our first simulation results show that for a fixed fluid parameter set and elongational rate the strain hardening indeed decreases if the solid area fraction increases starting from zero, in qualitative agreement with the behavior seen in experiments. In the presentation further results will be shown on the bulk extensional viscosity if the elongational rate (Weissenberg number) is increased.

Linear stability analysis of viscoelastic Couette flow using finite element method
Juliana V. Valerio and Marcio S. Carvalho
Department of Mechanical Engineering, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, RJ 22453, Brazil

The complete understanding of viscoelastic flows in many situations requires not only the steady state solution of the governing equations, but also its sensitivity to small perturbations. Linear stability analysis leads to a generalized eigenvalue problem. Solving the GEVP is challenging, even for Newtonian liquids, because the incompressibility constraint creates singularities that lead to a physical infinite eigenvalues. For viscoelastic flows, the difficulties are even higher because of the continuous spectrum of eigenmodes associated with differential constitutive equations. The Couette flow of UCM liquids has been used as a classical problem to address some of the important issues related to stability analysis of viscoelastic flows. The spectrum consists of two discrete eigenvalues and a continuous segment of eigenvalues with real part equal to -1/We (We is the Weissenberg number). Most of the numerical approximation of the spectrum of viscoelastic Couette flow presented in the literature were obtained using spectral expansions. The eigenvalues close to the continuous part of the spectrum show very slow convergence. In this work, the linear stability of Couette flow of UCM liquid was studied using Finite Element Method, which makes it easier to extend the analysis to complex flows. Different sets of basis functions were used to describe the elastic stress field and the results show the effect of the discretization on the ability to approximate the continuous part of the spectrum. A new procedure to eliminate the "infinite eigenvalues" from the GEVP that come from differential equations without a time-derivative term (continuity equation and momentum equation at Re = 0) is also proposed. The procedure takes advantage of the structure of the matrices involved and avoids the computational effort of common mapping techniques. With the proposed procedure, the GEVP is transformed into a smaller simple EVP, making the computations more efficient.

Viscoelastic stagnation point flow in a wake
Michael Renardy
Mathematics, Virginia Tech, Blacksburg, VA 24061-0123, United States

We investigate stagnation point flow of an Oldroyd B fluid away from a wall. For the axisymmetric case, an exact solution exists which has a quadratic velocity profile. For the planar case, the velocity is quadratic near the stagnation point, but grows exponentially at infinity.
Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Vermont PL2

Rheology and energy

Robert C. Armstrong

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Perhaps the greatest challenge facing humankind in the 21st century is to provide sustainable energy sources to meet the demands for quality of life and economic growth in both the developed and developing world. The need for addressing this energy challenge is greater than at any time in the recent past. This is driven by several factors that together constitute a "perfect storm" requiring our response. These drivers include supply and demand, security, and environmental concerns. Consider that over the next half century global energy use is expected to double and global electricity demand will be required. Security concerns are highlighted by the geographical and geopolitical realities of the locations of energy supplies and of the primary users of these resources, principally oil and natural gas. Finally, carbon dioxide emissions associated with combustion of fossil fuels are increasingly of central concern in global climate change. This concern will drive decisions about the evolution of the global energy system, namely whether it will evolve in a business-as-usual path or whether we will turn to less carbon intensive or carbon-neutral energy sources. I will discuss these factors and why they make a compelling case for devoting significant effort to energy now. I will then discuss areas where rheology can play a role in reducing energy demand or as an enabling science for new energy technologies.

Symposium SC
Suspensions, Colloids and Granular Materials

Organizers: Robert Butera and Jonathan Bender

Tuesday 9:45 Vermont SC16

Jamming of dense suspensions of uniform non-spherical colloids

Ryan J. Larsen, Jin-woong Kim, and David Weitz

DEAS, Harvard University, Cambridge, MA 02138, United States

Dense suspensions of non-Brownian particles are commonly observed to be shear thickening. As the concentration of particles increases, the increase in viscosity with shear rate shear often becomes more abrupt until, at the highest concentrations, discontinuous shear thickening is observed. In contrast to the typical behavior, some particle suspensions can display both continuous and discontinuous shear thickening (or jamming) in the same flow curve at a given volume fraction. Dense aqueous suspensions of polystyrene particles stabilized by various surfactants are observed to undergo a dramatic jamming transition at shear rates higher than the shear rates where continuous shear thickening occurs. When this jamming transition occurs in a rheometer equipped with a cone and plate geometry, the flow becomes irregular, tearing is observed in the sample, and solid-like granules may even churn out from the gap. This jamming transition is observed in both spherical and dumbbell-shaped particles. We also show that the continuous shear thickening portion, but not the jamming portion, of the flow curve can be eliminated by the reducing or nearly eliminating the stabilizing surfactant from the system. It appears therefore the continuous shear thickening is associated with particles stability, and that jamming is associated with particle instability.

Tuesday 10:10 Vermont SC17

Rheology and microstructure of shear thickening colloidal dispersions by flow-USANS

Dennis Kalman, Caroline Nam, and Norman J. Wagner

University of Delaware, Newark, DE 19716, United States

Shear thickening in particle suspensions is a problem in processing and coating industries; shear thickening fluids have also been utilized with ballistic fabrics in protective armor applications. Shear thickening is known to occur via the formation of load bearing hydroclusters from theory, simulations, flow-SANS experiments, and indirect rheological measurements. Here, a flow-USANS data set, in the radial direction (2,3- or gradient,vorticity-plane) in the low q regime of 3.3 x 10^-3 to 3.3 x 10^-1 Å^-1 of a model monodisperse, hard-sphere silica suspension in polyethylene glycol is studied. A dilute measurement is used to determine the particle form factor, which is used to determine effective structure factors of 3 concentrated samples (vol% = 20, 40, and 50) under flow in the low shear plateau, shear thinning, and shear thickening regimes. A
significant structural rearrangement is seen in the strongly shear thickening samples. These new microstructural measurements are used with previous flow-SANS and rheo-optical measurements and compared with theories for the structure of shear thickened colloidal suspensions. These measurements on this model suspension are used to further analyze a thixotropic, shear thickening fumed-silica suspension where both the particle structure and form factor are affected by shear thickening.

Tuesday 10:35 Vermont SC18

**A micromechanical approach to the rheological behavior of a suspension of particles in a Herschel-Bulkley fluid**

Xavier Chateau and Kien Luu Trung

*LMSGC, Navier Institute, Champs sur Marne 77420, France*

The rheological behavior of a suspension of non brownian particles dispersed in a yield stress fluid is studied within the framework of change of scale methods. The suspending fluid obeys a Herschel-Bulkley law characterized by its yield stress, its plastic viscosity and its plastic index. The particles are modelled as indeformable, neutrally buoyant spheres. Furthermore, it is assumed that brownian motion and inertial effects are negligible and that only hydrodynamic forces apply on particles (non colloidal suspension). First, the main features of the upscaling approach are recalled. Then, the overall behavior is looked for in the form of a relationship between the macroscopic stress and rate of strain tensors. Thanks to the fact that inertial effects are negligible, it is shown that the overall behavior can be determined from the solution of a heterogeneous rheology problem defined on a representative elementary volume in which the macroscopic rate of strain tensor plays the role of a loading parameter. A nonlinear homogenization method, initially developed to deal with heterogeneous plastic solids, is used to estimate the constitutive response of the suspension with overall isotropy. In this situation, the overall behavior is isotropic. Different estimates corresponding to different morphologies of the particle distribution within the suspending fluid are presented. In all the cases, the overall behavior of the suspension obeys Herschel-Buckley law too with a macroscopic plastic index equal to the fluid one. The global yield stress value depends only on the volume fraction of the particles and on the fluid yield stress while the global plastic viscosity value depends only on the volume fraction of the particles and on the fluid plastic viscosity. The prediction of the model are compared to experimental data found in the literature in order to, at first, highlight the efficiency of the method and, then, to identify the domains of validity of the different estimates.

Tuesday 11:00 Vermont SC19

**Flows of concentrated suspensions in symmetric and asymmetric bifurcations**

Chunguang Xi and Nina C. Shapley

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

Concentrated suspensions flowing in complex geometries are often encountered in materials processing applications such as injection molding and extrusion. One example of a practical complex geometry is a branching, or bifurcation flow. Previous work on the behavior of dispersed particles in branching flows has generally emphasized the finite-size case where the particle diameter is close to the branch width. Meanwhile, a high loading of small particles, where the suspension can be compared to a continuum material, and the resulting impact on the concentration and flow fields have not received as much attention.

In our study, suspensions of neutrally buoyant, noncolloidal spheres in Newtonian liquids undergo steady, pressure-driven flow in a rectangular channel (4:1 aspect ratio) that divides into two symmetric or asymmetric branches at a T-junction. Particle concentration and velocity profiles are obtained by nuclear magnetic resonance imaging (NMRI). We aim to determine the effect of the branching ratio, geometry, and flow direction (diverging or converging) on the observed concentration and flow fields, for particle volume fractions of 0.4-0.5 and low Reynolds numbers. Recent observations of dividing streamlines and concentration inhomogeneities between the two branches and the influence of particle and flow conditions will be presented.

Tuesday 11:25 Vermont SC20

**Local measurements of the constitutive law of a concentrated noncolloidal suspension through MRI**

Guillaume Ovarlez, François Bertrand, and Stéphane Rodts

*Laboratoire des Matériaux et Structures du Génie Civil, Institut Navier - CNRS - LCPC, Champs sur Marne, France*

We study the behavior of dense suspensions of noncolloidal particles through Magnetic Resonance Imaging techniques. We measure the local velocity and concentration profiles in a Couette geometry, and also perform macroscopic rheometric experiments.

We observe that the flow is localized at low velocities. We study the short time response to a velocity step, and deduce from the measurements that dense suspensions have nevertheless a purely viscous behavior, without any observable influence of a yield stress or granular friction. As localization at low velocities induces the formation of a "jammed" zone, we argue that localization consists of a change in configuration at the grain scale in this jammed zone, whereas the flowing behavior remains purely viscous.

We also observe that the material is inhomogeneous under flow. We find that the shear-induced migration process at the origin of this inhomogeneity is almost instantaneous in contrast to other observations. Our results imply that the diffusion coefficients depend strongly on the concentration.

From the concentration and velocity profiles, we provide for the first time local measurements of the concentration dependence of viscosity, and find a Krieger-Dougherty law to apply. Importantly, our measurements are based on the true local shear rate and the true local concentration. We are also able to measure locally the maximum packing fraction.
We finally propose a simple constitutive law for dense suspensions, based on a purely viscous behavior, that accounts for all the macroscopic and local observations.

Symposium EP
Rheology and Structure of Entangled Polymer Systems
Organizers: Monty Shaw and David Venerus

Tuesday 9:45 Massachusetts  
Thermodynamics of non-isothermal polymer flows: Experiment, theory, and simulation
Tudor C. Ionescu¹, Brian J. Edwards¹, David J. Keffer¹, and Vlasis Mavrantzas²
¹Chemical Engineering, University of Tennessee, Knoxville, TN 37996, United States; ²University of Patras, Patras, Greece

We provide a critical evaluation of the so-called Theory of Purely Entropic Elasticity, which states that the free energy change of a flowing, non-isothermal viscoelastic fluid is entirely due to entropic effects, and contains no contributions due to elastic energy changes. Our investigation consists of both theoretical and experimental parts. In the theoretical part, we perform non-equilibrium Monte Carlo simulations to calculate both the energetic and entropic contributions to the free energy of the material under uniaxial elongational flow. This results in measurable energetic effects at higher strain rates, and these effects increase as temperature decreases. Experimentally, we measured the heat capacity at constant volume of LDPE under steady-state shear and uniaxial elongational flow conditions, and calculated the conformational contribution to this quantity. According to the Theory of Purely Entropic Elasticity, the conformational contribution to the heat capacity should be negligible; however, significant non-vanishing contributions are measurable at high strain rates. Results are qualitatively consistent between theory and simulation.

Tuesday 10:10 Massachusetts  
Large strain requirements for strain induced crystallization
Deepak Arora¹ and H. H. Winter²
¹Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, United States; ²Chemical Engineering, University of Massachusetts, Amherst, MA 01003, United States

The effects of strain and Weissenberg number (We) are being investigated for isotactic poly (1-butene) in order to get a better understanding of dynamics of shear induced crystallization. Earlier similar studies with isotactic polypropylene gave surprising results that need confirmation with a second polymer. Transmission intensity measurement and optical microscopy are the tools used to study these effects. Transmission intensity under parallel polar (IVV) and cross polar (IHV) is a measure of turbidity and birefringence, respectively. Janeschitz-Kriegl's protocol is used to study the influence of flow on rate of crystallization (nucleation followed by growth) and growth of anisotropy. For experiments at We-values of 0.5, 1, and 2; we made sure that the shearing period does not overlap with crystal growth. Spherulitic growth is observed for quiescent crystallization under polarized microscopy. In case of strain induced crystallization, we observed spherulitic as well as oriented growth depending on the strain and We. Shear-induced crystallization requires a surprisingly large strain but seems to level off for the strains of 420 and higher, indicating a saturation criterion for crystallization.

Tuesday 10:35 Massachusetts  
Flow-induced crystallization of polybutene-1: From the low shear rate region up to processing rates
Jimmy Baert¹, Peter Van Puyvelde¹, and Florentin Langouche²
¹Department of Chemical Engineering, Katholieke Universiteit Leuven, Leuven 3001, Belgium; ²Solvay Central Laboratory, Brussels 1120, Belgium

In this work a new shear cell, developed at the Solvay Central Laboratory, is used to present a global view of shear-induced orientation in polybutene-1. The shear cell is a sandwich type cell in which the sample is uniaxially sheared between two oppositely moving glass windows, driven by a servomotor. It can be operated from the low shear rate region up to rates of 1500s⁻¹. Deformations up to a few hundred shear units can be achieved, which is typically what is realized in the outer layers during injection moulding. Windows and holes are provided in the equipment to view the flow-vorticity plane of the sheared sample. An optical train consisting of a modulated spinning laser allows monitoring the transmitted intensity (crystallinity) and the birefringence (orientation, anisotropy) during shear flow and subsequent crystallization. For different polybutene-1’s the transmitted intensity and birefringence values are presented throughout the complete crystallization process for varying levels of shear rate and shear strain and for several crystallization temperatures. At low shear rates the results show a gradual rise of anisotropy in the samples despite the maintenance of the spherulitic geometry. At higher shear rates, this is followed by a much sharper rise in birefringence accompanied by a characteristic upturn in the birefringence pattern during flow. This upturn is attributed to the formation of a "shear-induced structure" related to the presence of oriented precursors. Remarkable also is the evolution of transmitted intensity which shows a characteristic minimum. Scaling relations for characteristic crystallization times as a function of molecular parameters (molecular weight, molecular weight distribution) and processing conditions (crystallization temperature, shear rate, shear strain) are proposed for the experimental data.
The Society of Rheology 78th Annual Meeting, October 2006

Tuesday Morning

Tuesday 11:00 Massachusetts EP19

A study of the flow induced crystallization behavior of polyethylene in simple shear and high-rate uniaxial extension
Martín Sentmanat¹, Delgadillo Omar², and Savvas G. Hatzikiriakos²
¹Xpansion Instruments, Akron, OH, United States; ²Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC, Canada

The flow induced crystallization behavior of a series of linear and branched polyethylenes was characterized in both simple shear and uniaxial extension at temperatures near the melt state. The strong flow generated at high rates in uniaxial extension had a significant impact on the flow induced crystallization behavior of the linear polymers at temperatures just above the melt. Polymer crystallinity measurements were conducted on the polymer samples both before and after stretching. High-rate cessation of extension experiments were also performed at temperatures near the melt state in order to elucidate the retardation effect of crystallization on the relaxation behavior of the polymers.

Tuesday 11:25 Massachusetts EP20

A new equation to describe melt shear-thinning behavior
J.P. Ibar
Eknet Research Campus, Wallingford, CT 06492, United States

Starting from dynamic viscosity data in the melt, we show that complex viscosity, \( \eta^* \), can always be expressed as a function of the elasticity of the melt, \((G'/G^*)^2\). Plots of \((G'/G^*)^2\) vs \(G^*\), for a frequency sweep, are linearized by a double-exponential function which we can rewrite as: \(p1*(1-p2*exp(-G^*/p3))+p4*(1-exp(-G^*/p5))\), where \(p1,...,p5\) are curvefitting constants. The second term is used to define a reduced coupling frequency: \(w*=w/(p4*(1-exp(-G^*/p5)))\). Plots of \(\log(\eta^*)\) vs \(\log(w)\) are perfectly linear (intercept=\(a_0\), slope=\(a_1\)), all the way from the Newtonian region to the non-Newtonian region, thus describing shear-thinning behavior with a true power law formula: \(\eta^*=(10^{a_0})^*w^{a_1}\) with \(a_1\) negative, and perhaps taking discrete value among only: 1/2; 2/3; 3/4; 4/5; 5/6 etc., depending on the "degree of entanglement" between the macrocoils defined in the Eknet model of macromolecules interactive coupling. Discussion on the influence of temperature, molecular weight, disentanglement will be given during the presentation. Capillary viscometry will also be discussed, with the possibility to determine dynamic type of information directly from capillary viscosity data.

Symposium MR
Microrheology
Organizers: Patrick Spicer and Victor Breedveld

Tuesday 9:45 Connecticut MR1

Active and nonlinear microrheology in the large-probe limit: Direct vs. bulk effects
Todd M. Squires
Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, United States

In passive microrheology, the linear viscoelastic properties of complex fluids is inferred from the Brownian motion of colloidal tracer particles. Active (but gentle) forcing can be also be used to obtain such linear-response information, and less gentle forcing has recently been employed to probe nonlinear material properties. Here we address a variety of issues that arise in the context of this technique -- most generally, what exactly can be measured, and how can such measurements be interpreted? Using a model system (a large colloidal probe pulled through a dilute colloidal suspension), we examine the different sources of stress upon the probe particle, including both direct probe-bath collisions and rheological stresses from the bulk. We discuss the relationship between such measurements and the analogous macro-rheological measurements, drawing analogies with well-known macro-rheological phenomena whenever appropriate. Finally, we discuss simple modifications for active microrheology that would simplify the interpretation, or would allow further rheological information to be obtained.

Tuesday 10:10 Connecticut MR2

Experimental two-particle microrheology of quasi 2-D viscous systems and thin films
Vikram Prasad, Stephan A. Koehler, and Eric R. Weeks
Physics, Emory University, Atlanta, GA 30322, United States

Microrheology is often used to determine the viscoelasticity of materials such as polymer solutions, hydrogels and cells by tracking the thermal diffusion of tracer particles. For heterogeneous materials, where single particle microrheology breaks down, a modified technique known as two-particle microrheology has been established where motions of particles with varying spatial separations are correlated. In 2-D systems, this correlated motion decays as 1/R, and can be used to identify the long wavelength modes in the system, and therefore the bulk viscoelasticity. For quasi 2-D systems (such as protein molecules at an air-water interface), very few experimental verifications of theoretical predictions exist. By changing the surface viscosity of the interface, we observe a transition in the correlated motions of tracer particles, from 2-D dominated at high surface viscosity to 3-D bulk fluid dominated at low surface viscosity (V. Prasad et. al, submitted to Phys. Rev. Lett.). We also look at these correlated motions (of rod shaped bacteria, and spherical colloids as the tracer particles) in thin soap films, where the thickness of the bulk fluid
in contact with the interface is varied, in addition to the surface viscosity. We find that the thickness of the fluid layer is found to have an effect on the transition from 2-D to 3-D as well. Consequences for microrheology in interfacial systems are discussed.

Tuesday 10:35 Connecticut

**Laser tweezer microrheology of colloidal dispersions and gels**

Eric M. Furst, Myung Han Lee, and Alexander Meyer  
Chemical Engineering, University of Delaware, Newark, DE 19716, United States

We study the microscopic response of colloidal dispersions and gels by manipulating single probe particles using optical tweezers. For this work, we use fluorescent polymethylmethacrylate (PMMA) dispersed in mixtures of decalin and cyclohexylbromide, with a refractive index and density closely matched to that of PMMA. The strength of attraction between particles is controlled by the concentration of a non-adsorbing polymer, polystyrene. In the absence of depletion, we measure the microviscosity of the suspension by translating the probe particle. The probe response is correlated with local structural transitions using confocal microscopy. In the presence of sufficiently strong attractive forces, particles aggregate to form a colloidal gel. In this case, we characterize the local and average strain fields, which depend on the probe oscillation amplitude and strength of depletion interactions. This work provides important insight into the manner in which stress is transmitted through a gel microstructure.

Tuesday 11:00 Connecticut

**Non-Brownian microrheology of a fluid-gel interface**

Erik K. Hobbie¹, Sheng Lin-Gibson¹, and Satish Kumar²  
¹NIST, Gaithersburg, MD, United States; ²University of Minnesota, Minneapolis, MN, United States

We use stroboscopic video microscopy to study the stability of a planar fluid-gel interface under simple steady shear flow. External noise plays a role analogous to temperature, but with periodic fluctuations associated with the repeated build-up and release of stress. From the motion of the interface, we extract the rheological properties of the underlying gel, pointing toward potential applications in the area of non-Brownian optical microrheology.

Tuesday 11:25 Connecticut

**In-situ monitoring of mechanical properties during photopolymerization with particle tracking microrheology**

Ryan P. Slopek and Victor Breedveld  
School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

Photopolymerization has a wide range of applications, which encompass the automotive, electronic, medical, optical, and coating industries. The fundamentals of the photopolymerization process, however, are not well understood. As a result, spatial variations of photopolymerization impose significant limitations on applications in which a high spatial resolution is required.

To address this issue, microrheology was employed to perform in-situ monitoring of the liquid-to-gel transition during free-radical photopolymerization. Photosensitive acrylate resins were exposed to ultraviolet light, while the Brownian motion of micrometer sized, inert fluorescent tracer particles was tracked via optical videomicroscopy. Statistical analysis of particle motion yielded the rheological properties of the embedding medium as a function of time and location, thereby relating UV exposure to the progress of polymerization and gelation.

Microscopy enabled a detailed study of three-dimensional gelation profiles. In addition, the effect of varying photoinitiator concentration, monomer composition, and light intensity was studied. Significant changes in gelation time were observed with increasing UV penetration depth into the sample. Post UV exposure reactions were investigated by placing a high-speed shutter in the path of the UV light, which allowed for accurate measurements of the progress of photopolymerization as a function of penetration depth and UV exposure time. In addition, the process of shrinkage was investigated using a high-resolution lithographic mask. By varying the illumination area, spatial effects of gelation-induced shrinkage were examined.

The microrheological study provides new and unique information previously unattainable by other methods used to study photopolymerization, which can potentially provide better control and a more complete understanding of the photopolymerization process.
When a droplet approaches a solid surface, the thin liquid film between the droplet and the surface drains until an instability forms and then ruptures. In this study, we utilize microfluidics to investigate the effects of film thickness on the time to film rupture for water droplets in a flowing continuous phase of silicone oil depositing on solid poly(dimethylsiloxane) (PDMS) surfaces. The water droplets ranged in size from millimeters to microns, resulting in estimated values of the film thickness at rupture ranging from 600 nm down to 6–nm. The Stefan-Reynolds equation is used to model film drainage beneath both millimeter- and micron-scale droplets. For millimeter-scale droplets, the experimental and analytical film rupture times agree well, while large differences are observed for micron-scale droplets. We speculate that the differences in the micron-scale data result from the increases of the local thin film viscosity due to confinement-induced molecular structure changes of the silicone oil. A modified Stefan-Reynolds equation is used to account for the increased thin film viscosity for the micron-scale droplet drainage case.

Torsional flow between parallel disks is an invaluable tool for investigating the rheological behavior of complex fluids. However, time-dependent measurements are often affected by torsional and axial transducer compliance, making it difficult to isolate the behavior of the fluid. At present, the only analyses of these effects are based on Newtonian fluids. In this study, we explore the effects of transducer compliance for torsional flow of viscoelastic fluids. This analysis is based on a perturbation solution to a time-dependent, two-dimensional self-similar flow of an ideal viscoelastic fluid. We find that the effect of torsional compliance on both shear stress and the first normal stress depended only on the ratio of fluid relaxation time to transducer torsional response time. Moreover, the effect of axial compliance depended both on the ratio of fluid to axial transducer response times as well as the level of fluid elasticity. Strong coupling effects were observed between axial and torsional compliance. Comparisons with available experimental data showed qualitative agreement with the model predictions derived in this study.

Extending the simulation model by Hyun et al. (2004) which had successfully produced the transient solutions of the dynamics in non-isothermal film blowing process for the first time in more than 30 years since the seminal modeling work by Pearson and Petrie (1970), to also cover additionally the flow-induced crystallization phenomenon occurring in the film, this study reports the first transient solutions of the dynamics in this expanded system. The stability analysis of the same system reveals the interesting effects of various process and material parameters such as cooling of the film, film draw ratio and fluid viscoelasticity, on the dynamic behavior of the film blowing process. The simulation model is validated by the transient solutions of the isothermal film blowing process reported in previous studies. The results are in qualitative agreement with the transient solutions of the dynamics in this expanded system. The stability analysis of the same system reveals the interesting effects of various process and material parameters such as cooling of the film, film draw ratio and fluid viscoelasticity, on the dynamic behavior of the film blowing process.
were performed to characterize the rheology of the paste before and after the extrusion. Wall slip of paste is also measured experimentally in order to be used as a boundary condition in the flow simulations. Finite element simulations are performed to predict variations of the extrusion pressure with apparent shear rate and die geometrical characteristics and these results are compared with experimental findings. Finally, the degree of fibrillation is used as a microscopic predictive parameter that is compared with the experimentally determined tensile strengths of the extruded samples.

Tuesday 11:25 Rhode Island

A molecular approach to fully eradicate sharkskin extrude distortions in entangled polyethylene
Juan F. Vega\textsuperscript{1}, María T. Expósito\textsuperscript{2}, and J Martínez-Salazar\textsuperscript{2}

\textsuperscript{1}Departamento de Química Orgánica I, Universidad Complutense de Madrid, Madrid 28040, Spain; \textsuperscript{2}Departamento de Física Macromolecular, Instituto de Estructura de la Materia. CSIC, Madrid 28006, Spain

Flow instabilities during processing are typical features of polymeric fluids, but especially significant in entangled polyolefins with a narrow molecular weight distribution. The elimination of the distortions has been the scope of several studies along the last decades. Our more recent work points towards the fact that the addition of very small amount of UHMWPE effectively removes distortions during extrusion of linear metallocene polyethylene (mPE). Interesting results have been obtained for melt-mixed [Aguilar et al. et al. J. Polym. Sci., Phys. Ed.\textit{43}, 2963-2971 (2005)] and solution-mixed [Aguilar et al. Macromolecules \textit{37}, 681-683 (2004)] blends of a mPE with small amounts of UHMWPE. As UHMWPE is introduced, an enhanced elastic character of the polymeric system develops, which is much more pronounced in the solution-mixed blends. In addition, the defects on the extrudate surface diminish with the addition of UHMWPE for the melt-mixed sample, but completely vanish in the solution-mixed blend. In this communication, we present further results on the use of very small amounts of high molecular weight polyethylene as a route for the elimination of distortions in mPE. We have evaluated the physical properties and capillary flow behaviour of blends of a mPE with linear PE samples of different molecular features. The effects of both molecular weight and concentration of this second component have been evaluated. The results obtained suggest the existence of a critical molecular length for the elimination of distortions at a given concentration.

Symposium PP

Paper, Pulp and Industrial Processes

Organizers: Douglas Bousfield and Albert Co

PP1

Effect of strongly repulsive particle interactions on the rheology of concentrated silica suspensions

Saeid Savarmand\textsuperscript{1}, Pierre J. Carreau\textsuperscript{2}, François Bertrand\textsuperscript{2}, and David J.-E. Vidal\textsuperscript{1}

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The relationship between particle interactions and rheological properties of charge-stabilized mono- and bidisperse aqueous silica suspensions at very low ionic strengths was investigated. A Maron-Pierce-like model for correlating the apparent yield stress to solids content was used to specify experimental freezing and maximum packing fractions. The freezing volume fractions were corrected for polydispersity and an equivalent hard-sphere maximum packing was determined for each suspension. The apparent yield stress of concentrated suspensions was further correlated with particle zeta potential through an effective particle diameter. Correlation for various volume fractions and blend ratios led to the determination of a hydrodynamic scaling parameter, function of solids content and blend ratio. Also, shear viscosity data at 100 \textit{s}\textsuperscript{-1} showed a hard-sphere behavior with the largest maximum packing fraction for a 50/50 bidisperse suspension.

PP2

Rheological aspects of paper coatings

John Husband and Rajan Iyer

Imerys, Sandersville, GA, United States

Paper coatings form the functional layer that is applied on paper surfaces to impart certain attributes that make it suitable for a desired end-use. Typically paper coatings give a smooth surface, brightness and opacity, gloss and excellent print performance to the raw paper. Minerals form a majority of the water-based suspensions that are commonly used as paper coatings. Minerals used are Kaolinite clay, Calcium Carbonate (both in ground natural form and precipitated crystalline form), talc, Titanium Dioxide and others.

The rheological behavior of paper coatings is crucial to application performance. Different methodologies are employed to apply these suspensions on to paper. The shear and elongational flows under dewatering conditions dictate the evenness of the coating layer as well as the defect free operation of the coater.

In this work the various application methods used in coating paper are discussed with a rheological perspective. Also discussed are the shear rate regimes prevalent during such operations. Some of the new methods like high speed curtain coating of paper are discussed and the challenges outlined. Typical methods used to characterize coatings under various shear and elongation strain conditions are also discussed.
Simulating and improving the application behavior of paper coatings by rheological test methods

Joerg Laeuger¹ and Santtu Hietala²

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New processing conditions like higher speeds and the demand for ongoing quality improvements in the paper industry lead to the need of a deeper understanding of the rheological phenomena involved in the coatings of papers. Four different test methods are proposed which provide insight into different aspects of the complex rheological behavior of paper coatings. 1. Oscillatory measurements are used to measure the rest structure, which gives information on the long term stability at rest and on the stability during transportation of paper coatings. 2. Measurements at high shear rate reveal information about the stability of the coating at the high shear conditions, which are experienced at the blade in blade coating. 3. The right time frame of the structure build up after the high shear rate conditions at the blade, i.e. the thixotropy, is an important parameter influencing the quality of the final product. The structure build up can be measured in a so-called 3 interval thixotropy test. 4. For the evaluation of the dewatering and immobilization of the paper coating a special immobilization cell is used in which different combinations of paper and paper coatings can be tested. With the help of the tests described it is possible to simulate the real processing conditions as close as possible. All tests can be used in research and development for improvements in coating formulations as well as a fast and easy way to perform quality control measurements. The new methods can serve as tools to reduce the amount of expansive and time consuming machine trials significantly.

The influence of dispersant chemistry on calcium carbonate suspension rheology

Gerard Gagnon, David J. Neivandt, and Douglas W. Bousfield

Chemical and Biological Engineering, University of Maine, Orono, ME, United States

The rheology of high solids paper coatings is critical in terms of the ability to apply the coatings to paper at high speeds. Coatings often contain pigments, latex binders, soluble polymers, and other additives. The influence of dispersants on the rheological properties is known to be important from empirical measurements, but a good understanding of the mechanisms is lacking. Especially for coatings that contain calcium carbonate pigments; the role of the calcium ion can influence the behavior of the dispersant. A precipitated calcium carbonate pigment was dispersed with six different polyacrylate based dispersants. These dispersants had different molecular weights and different charge densities. The steady shear and oscillatory shear behavior was characterized by controlled stress rheometers. High shear rate viscosities were obtained with a concentric cylinder rheometer. The concentration of calcium ion in the liquid phase was characterized by a titration method. The concentration of the dispersant in the liquid phase was characterized by an infrared absorption measurement. The different dispersants were found to have a different affinity towards the calcium ion. The molecular weight had a minimal influence on this affinity. The amount of dispersant adsorbed at the pigment surface was found to change with dispersant type. The rheology of the different suspensions was compared at the same solids level.

Effects of fiber shape on fiber settling dynamics

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We employ laboratory experiments and simulations to examine the effects of fiber shape on the dynamics of rigid fibers sedimenting in quiescent fluids. Sedimentation trajectories for many fiber shapes and initial orientations were recorded using a digital video imaging system. Trajectories are also predicted using simulations with various levels of approximations for the intrafiber hydrodynamic interactions. All simulations of the sedimentation dynamics agree qualitatively with those observed experimentally. Quantitative differences for the various approximations are discussed. The observed behavior is interpreted in terms of the effects of three dimensional shape features on fiber motion.
A thermodynamically consistent model for the thixotropic rheological behavior of concentrated colloidal star polymer solutions

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In this work we report a new model for the rheological thixotropic behavior of colloidal star polymer solutions. Given the excellent capabilities of controlling the molecular structure, star polymers constitute an ideal system for exploring the soft matter rheology. The stars exhibit dual, colloidal and polymeric behavior manifested in several physical properties and in particular their relaxation and flow. Detailed optical and rheological experiments have revealed the interplay between their molecular microstructure and their macroscopic rheological properties often characterized by viscoelasticity (yield stress) and thixotropy (time dependent rheological behavior)\cite{1}. In the present work we use them as a model system in order to better understand thixotropy. Thixotropy is typically modeled phenomenologically as a structurally-dependent viscoplastic behavior \cite{2}. However, the resulting models are often restricted to simple shear flows and are not presented in a form that can be shown do be consistent with nonequilibrium thermodynamics. In the present work we present a new thixotropy model for a well-defined system of colloidal star polymer suspensions that is based on previous ideas from the description of polymeric liquid crystals and viscoelasticity. As a result, the model is presented in a thermodynamically admissible form, which is also generally applicable to arbitrary flows. In addition, the model parameters are connected to the system's molecular microstructure. A comparison of the model's predictions against rheological and optical (DLS) experiments allows for the first time a direct connection of rheology to the system's microstructure for a system exhibiting yield stress and thixotropy.


Yielding, strain softening and shear thinning in dense colloidal suspensions, gels and glasses

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A microscopic statistical dynamical theory for the effect of deformation on the transient localization length, elastic modulus, alpha relaxation time, shear viscosity and other dynamic properties of glassy colloidal suspensions and polymer-particle depletion gels has been developed \cite{1,2}. The approach is built on activated barrier hopping as the elementary physical process in conjunction with the simple idea that deformation distorts the confining nonequilibrium free energy. The relative roles of mechanically driven motion versus thermally activated viscous flow on the nonlinear rheological behavior has been studied. For glassy hard sphere suspensions power law and/or exponential dependences of the elastic modulus and yield stress on colloid volume fraction are predicted. For polymer-particle suspensions the cage constraints and depletion bond strength are quantified using the accurate Polymer Reference Interaction Site Model theory of structure \cite{3}. The absolute yield stress collapses onto a universal master curve as a function of the polymer concentration (colloid volume fraction) when scaled by its ideal mode-coupling theory nonergodicity transition value, and sufficiently deep in the gel is of an effective power-law form with a universal (nonuniversal) exponent. Flow curves show an intermediate shear rate dependence of an effective power law form, becoming more solid-like with increasing depletion attraction. Qualitative and quantitative comparisons of the theoretical results with experiments show encouraging agreement, and multiple testable predictions are made.


Rheology of soft particle pastes: Macroscopic behavior and microscopic origins

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Soft particle pastes (SPP) are concentrated suspensions or emulsions of soft, deformable particles compressed against one another. Soft particle pastes appear in ceramic processing, coatings and food and cosmetic products. Types of particles making up a SPP include microgels,
compressed emulsions, polymer-coated sand and star polymers and micelles. These dense suspensions behave like complex fluids and have interesting flow properties. They are shear thinning, have a yield stress, show normal stresses, aging and memory and also exhibit slip at smooth shearing surfaces. Here we present a computational methodology to study the rheology of SPPs and results of a theoretical study using the simulation.

We model SPPs as a concentrated suspension of elastic spheres. The particles are packed against one another and interact through strong elastohydrodynamic lubrication forces generated due to compression and relative motion between them. The 3D molecular dynamics-like simulations capture the particle dynamics and also its effect on bulk rheology. Constant stress and constant shear-rate simulations are used to define the complete stress tensor of these materials. The simulation results for the yield, shear and normal stresses are presented as function of concentration and the ratio of viscous to elastic forces. The macroscopic rheology of these materials is related to the microstructural changes that occur during and upon cessation of flow. The theoretical predictions of the bulk rheology are found to compare favorably to previous experimental observations. Use of the simulation as a model for micro rheology of complex fluids is discussed as well as preliminary results on aging and memory of soft particle pastes.

**Tuesday 2:45 Vermont**

**Soft polymer particle suspensions with controlled particle surface morphology**

Gerald H. Ling¹ and Montgomery T. Shaw²

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Polymer additives in fluids are used in a wide range of industrial applications. The low mass concentration required to induce a significant change in rheological properties is of great technological importance. An especially complex and important case is that of solvent-swollen polymer particles suspended in the swelling fluid. Emphasis in literature has mainly been limited to systems with aqueous fluids and little is known of systems comprising soft particles in organic fluids. We report the rheological and microstructural investigation of dispersions of crosslinked microparticles (CPMs) vs. block-copolymer micelles in Newtonian organic fluids. The effect of particle size and surface morphology on the steady-shear viscosity as a function of temperature is explored using conventional rotational and oscillatory rheometry. The results are compared to previous model systems on soft-particle dispersions. Particle size reduction was achieved through the use of both mechanical and chemical means while surface morphology was controlled by the removal of surface terminal chains.

**Tuesday 3:10 Vermont**

**Anomalous temperature behavior of colloidal silica gels in low-MW polyethers**

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Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905, United States

Dispersions of hydrophobic and hydrophilic silica (fumed) nanoparticles in various low molecular weight (MW) polyethers are systematically studied in order to understand the factors dictating the nature and magnitude of colloidal interactions in the systems. In particular, dynamic rheological experiments are employed to characterize the effects of temperature on the properties of the dispersions. We find that the elastic modulus of hydrophobic silica in poly(ethylene glycol) dimethyl ether (MW = 250 g/mol), PEGdm(250) gels increases irreversibly after heating from 25 to 80 °C, whereas the elastic modulus of hydrophobic silica in PEGdm(250) decreases reversibly with temperature. The effects of time and silica concentration are also evaluated for samples that have been thermally treated and compared to those tested at room temperature. At 80 °C, the elastic modulus of the hydrophilic silica in PEGdm(250) increases as a function of time and reaches a plateau value after ~200 min. At lower concentrations of hydrophobic silica in PEGdm(250) (starting at 2 wt%), the relative increase in elastic modulus with temperature becomes larger. This anomalous increase in elastic modulus with temperature can be attributed to a condensation reaction between the silanol groups on the silica surface and the PEGdm(250) molecules that takes place upon heating, as verified by thermogravimetric analysis. The amount and type of end groups present in the polyethylene glycol (PEG) and methyl end capped analogs, PEGdm and PEGm used in this study seems to dictate the occurrence of this reaction.

**Tuesday 4:00 Vermont**

**Transitions in a vibrated/stirred granular flow**

James F. Gilchrist, Kenneth J. Ford, and Hugo S. Caram

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We investigate flow of powders within a model high shear granulation process. High shear granulators typically produce flow by sweeping a pitched bladed under a granular bed at high rotation rates, providing both fluidization from upward lift from fast moving blades and flow in a circular motion. In our experimental setup, we partially decouple the fluidization and circulation by independently vibrating and stirring a deep granular bed. Vibration is driven by a solenoid with a sinusoidal power input. Without stirring, vibration begins to fluidize the bed when the Froude number, Fr > 1. By attaching an accelerometer to the vessel, we measure the resulting time of flight. The deep granular bed primarily behaves as a solid mass at moderate Fr, and we compare the accelerometer data to a simple model of a bouncing mass on a spring. The stirring mechanism is a four-sided vane tool, similar to that used in rheology and the ASM standard for soil mechanical testing, and the driving mechanism allows measurement of the power required to maintain a constant rotation rate. Without vibration, the power draw is linearly related to the rotation rate. At high Fr, the power requirements for stirring the fluidized bed decrease dramatically. At intermediate Fr, we observe a transition between dense granular flow and fluidized granular behavior with increased vibration and stirring by monitoring the power.
requirements for stirring. This transition marks the boundary between dense granular flow and fluidized granular flow, and suggests the degree to which stirring influences bulk fluidization.

Tuesday 4:25 Vermont SC27

**Cage dynamics and dynamical heterogeneity in uniformly heated granular media**

Rohit A. Ingale\(^1\), Pedro M. Reis\(^2\), Guillaume Marty\(^3\), and Mark D. Shattuck\(^1\)

\(^1\)Benjamin Levich Institute, City College of New York, New York, NY 10031, United States; \(^2\)PMMH, Ecole Supérieure de Physique et de Chimie Industrielle, Paris, France

Granular materials exhibit jamming transition which resembles the well known glass transition observed in glass-forming liquids and colloids. This has generated considerable interest in studying granular media for better understanding of glassy and "jammy" materials in general.

We thus report a novel experimental investigation of the dynamics of quasi-2D granular fluid, under homogeneous thermalization via vertical vibration. The typical trajectories of the grains display the so-called cage effect and are remarkably similar to the ones observed in experiments with colloids and molecular dynamics simulation of glass formers. We study the cage dynamics by employing the Mean Square Displacement (MSD) and the Self Intermediate Scattering Function (SISF), which are standard tools to probe colloidal and molecular systems. The granular media displays dramatic slowing down of dynamics as the particle filling fraction is increased towards crystallization/jamming. Moreover, the relaxation time extracted from the SISF, as a function of filling fraction, is described in good agreement by the Vogel-Fulcher law which is common for many glass forming systems. The SISF displaying slower than exponential relaxation suggests dynamic heterogeneity and possibility of a relevant dynamical length scale. We further employ multi-point dynamic susceptibilities to quantify the correlated nature of the dynamics and identify growing dynamic correlation length scales. We believe our experimental results are an important step in providing new insight on the dynamical behavior of dense granular materials as well as colloidal/molecular glassy systems.

Tuesday 4:50 Vermont SC28

**Mean-field theory of glass transitions**

Michio Tokuyama

Institute of Fluid Science, Tohoku University, Sendai, Japan

The mean-square displacements obtained in experiments and simulations near the glass transitions are analyzed by employing the mean-field theory recently proposed by the present author (Physica A 364, 23-62 (2006)). By comparing different glass transitions with each other from a unified point of view, it is shown that the mean-square displacements obey a logarithmic growth in a fast beta stage and a power-law growth of a super-diffusion type in a slow beta stage. It is also shown that the long-time self-diffusion coefficients are described by a non-singular function of a control parameter for any types of glass-forming systems, leading to no divergence of any characteristic times at the glass transition. The remarkable similarities are then found in various physical quantities, including the free volume. It is thus shown from a unified viewpoint based on the mean-field theory how one can predict a supercooled point over which the supercooled liquid appears and the glass transition point theoretically. The present theory provides a useful tool to understand the different glass transitions. The experimental systems analyzed here are a suspension of neutral colloids and suspensions of magnetic colloids, while the simulations are a hard-sphere fluid and a Lennard-Jones liquid.

Tuesday 5:15 Vermont SC29

**Thixotropy and yield stress behavior of drilling fluids**

Jason Maxey

Global R&D, Baker Hughes Drilling Fluids, Houston, TX 77073, United States

Drilling fluids have long been recognized as complex fluids which exhibit both yield stress behavior and varying degrees of thixotropy. Traditional models for yield stress behavior have long been used, with the Bingham plastic model remaining prevalent for description in the field and the Herschel-Bulkley model becoming the standard for computer simulations of fluid behavior. Neither of these models represents the full behavior of drilling fluids, either missing aspects of the shear-thinning behavior or inaccurately predicting the yield stress of the fluids. These errors are exacerbated through variations in measurement techniques by technicians who do not fully appreciate the thixotropic nature of these fluids. An improved understanding of the rheological behavior, in particular the yield and thixotropic nature, of drilling fluids would result in improved models and enhanced drilling performance, thereby reducing drilling costs.

An examination of some typical drilling fluids will be presented. The entwined effects of thixotropy and yield stress on rheological measurements will be highlighted. These fluids will also be evaluated with traditional yield stress models as well as with several recently proposed yield stress models.

Tuesday 5:40 Vermont SC30

**A model for ageing dynamics in laponite suspensions**

Yogesh M. Joshi

Department of Chemical Engineering, Indian Institute of Technology- Kanpur, Kanpur, UP 208016, India

Laponite, a hectorite clay, when dispersed in water forms Wigner glass at concentrations as low as 1 volume %. It is observed that after dispersing the laponite in water, characteristic time of the system increases exponentially with its 'age' followed by a linear increase as system enters a nonergodic state [1]. It is proposed that the rapid increase of characteristic time of the system is due to diffusion of laponite particles to
fill the space. Consequently the 'cage' is formed and system enters full ageing regime where characteristic time increases linearly with age. A simple scaling model is developed to predict this behavior that is in reasonable agreement with the experimental observations.


**Symposium EP**
**Rheology and Structure of Entangled Polymer Systems**
Organizers: Monty Shaw and David Venerus

**Tuesday 1:30 Massachusetts**

**Flow instabilities and constitutive relation in entangled polymer solutions studied by particle tracking velocity**
Y. Thomas Hu and Alex Lips
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The velocity profile in Couette as well as cone and plate geometries was measured using high spatial resolution particle tracking velocimetry for two entangled polymer solutions under steady shear flow. Shear banding type of flow instability was observed after the stress maximum for the solution with the larger entanglement density $Z = 30$. The steady state velocity profile was nonlinear as was observed by Tapadia (PRL 96, 016001). Possible origins of the nonlinearity were investigated. Local shear rate data were extracted from the velocity profile in Couette geometry and used to construct the constitutive relation, which is believed to be much more accurate than that measured by conventional rheometry since the common errors due to wall slip and edge fracture were largely avoided. The constructed constitutive relation shows a stress plateau with finite slope, which decreases with the increase of the entanglement density.

**Tuesday 1:55 Massachusetts**

**A first determination of velocity profile of entangled polymer solutions in sliding plate rheometer**
Pouyan E. Boukany and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

In this work we attempt to answer several key questions concerning the flow characteristics of entangled polymer solutions in a sliding plate shearing cell. We explore (a) how the molecular weight distribution affects the velocity profile in simple shear, (b) whether the observed shear banding is consistent with a non-monotonic constitutive model, (c) whether the flow response and velocity profiles are different in simple shear depending on the different modes of shear. Our results provide an interesting comparison with a recent report on a polydisperse [Tapadia and Wang, Phys. Rev. Lett. 96, 016001 (2006)] revealing the first evidence that entangled polymers may not be able to respond homogeneously to a startup shear in cone-plate flow geometry of a rotational rheometer. For example, using a highly monodisperse sample, we observed the sample to partition into two fractions with very different local shear rates instead of possessing a smooth spatial variation of the local shear rate as seen for the polydisperse sample. In the stress plateau, the shear banding appears to involve different local shear rates instead of just two values. This shear banding like profile was also seen to convert to linearity upon switching to the constant force mode.

**Tuesday 2:20 Massachusetts**

**Simulation of apparent wall slip in entangled polymer melts using a full-chain stochastic tube model**
Fang Xu$^1$, Morton M. Denn$^1$, and Jay D. Schieber$^2$

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Entangled melts and solutions of linear polymers exhibit apparent wall slip at high shear rates. Bergem [1] seems to have been the first to suggest that disentanglement of wall-region chains from chains in the bulk is the mechanism for apparent slip, and this mechanism is now widely accepted, at least at rates below the "slip-stick" transition, although agreement is not universal [2]. We report here on simulations of shear flow near a wall employing a full-chain stochastic tube model for entangled melts and solutions of linear polymers; the model requires only one adjustable parameter (equivalent to the Rouse time) in bulk flow [3]. The surface density of chains is also required as an input when the model is used to simulate both free chains and chains that are tethered to the wall. The computed results for the wall slip velocity and slip length are in good agreement with experimental data on the flow of a polydimethylsiloxane melt over tethered polydimethylsiloxane chains by Durliat et al. [4]. There is a significant decrease in the computed entanglement density of wall chains when apparent slip occurs.

Organoclay has been added to similarly entangled solutions at loadings of 0.89 and 2.68 wt% relative to solvent. Pure organoclay dispersions of modified montmorillonite clay from which excess free surfactant has been removed, and solutions are comprised of high molecular weight, narrow molecular weight distribution polystyrene ($M_n = 8.42 \times 10^6$ g/mol), organically modified montmorillonite clay from which excess free surfactant has been removed, and $p$-xylene. The polymer concentration has been fixed $p$-xylene. The polymer concentration has been fixed

Large amplitude oscillatory shear (LAOS) is a most effective protocol to interrogate the nonlinear flow behavior of viscoelastic materials. With an oscillation frequency exceeding the internal relaxation rate, the sample would necessarily respond solid-like. With sufficiently high amplitude in the LAOS, the sample necessarily behaves like a solid subjected to large deformation. How can or cannot the sample experience homogenous strain? Besides the initial observations[1] of the LAOS behavior of polydisperse entangled polymer solutions, we show a wider array of flow instabilities and shear banding in monodisperse samples. Depending on the amplitude, the development of highly nonlinear strain deformation across the sample thickness can occur either through a gradual diffusive process or rapidly with immediate appearance of a faulty plane as an indication of network disintegration. Detailed features will be illustrated to demonstrate the necessity to open up the "black box" and the implications for all the rheological studies in literature involving LAOS.


**Nonlinear behavior in large amplitude oscillatory shear of entangled polymers**

Sham Sundar Ravindranath and Shi-Qing Wang

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

Tuesday 2:45 Massachusetts EP24

Large amplitude oscillatory shear (LAOS) is a most effective protocol to interrogate the nonlinear flow behavior of viscoelastic materials. With an oscillation frequency exceeding the internal relaxation rate, the sample would necessarily respond solid-like. With sufficiently high amplitude in the LAOS, the sample necessarily behaves like a solid subjected to large deformation. How can or cannot the sample experience homogenous strain? Besides the initial observations[1] of the LAOS behavior of polydisperse entangled polymer solutions, we show a wider array of flow instabilities and shear banding in monodisperse samples. Depending on the amplitude, the development of highly nonlinear strain deformation across the sample thickness can occur either through a gradual diffusive process or rapidly with immediate appearance of a faulty plane as an indication of network disintegration. Detailed features will be illustrated to demonstrate the necessity to open up the "black box" and the implications for all the rheological studies in literature involving LAOS.

Tuesday 3:10 Massachusetts EP25

**Secondary stress overshoot of polymer solution with bimodal molecular weight distribution in strong shear flows**

Haibo Qi1, Mohammad Islam2, and Lynden Archer1

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Unusual secondary overshoots appear both in shear stress and first normal stress difference (N1) during fast shear flows of entangled polymer blend solutions with widely separated molecular weight. We use a combination of optical birefringence experiments and theory to investigate the start-up of shear flow of polystyrene linear/linear and polybutadiene branched/linear blend solutions. In accordance with experimental observation, the model predicts that transient stretching of the faster relaxing blend component is responsible for the early time overshoot. Transient stretching of the slower relaxing species is likewise found responsible for the second overshoot. We focus on the role of the characteristic time scales of blend components on the appearance of the secondary overshoot, and discuss consequences for strain hardening in entangled polymer blends subject to extensional flows.

Tuesday 4:00 Massachusetts EP26

**Fast shear of binary blends of polymer melts: New constitutive models and experimental results.**

Kamakshi Jagannathan1, Dietermar Auhl1, Daniel J. Read2, Alexei E. Likhtman3, Richard S. Graham1, Jorge Ramirez2, and Tom C. McLeish1

1Polymer IRC, University of Leeds, Leeds LS2 9JT, United Kingdom; 2Applied Mathematics, University of Leeds, Leeds, United Kingdom

In linear rheology of entangled polymers mixing rules are relatively well established - from empirical double reptation to more sophisticated tube dilution and constraint release theories. In non-linear rheology however the situation is quite different - so far no molecular constitutive equation is generalized and rigorously tested for the case of binary blends. In this talk we propose a new class of constitutive models for polymer blends, consisting of $n^2n$ equations where $n$ is number of blends components. We implement this idea on 2 levels of details - in terms of simple Role-Poly equation for stress only and in terms of full tube CCR theory. In order to test these new equations, we performed start-up shear experiments on binary polyisoprene blends with wide separation of relaxation times. We used preliminary theory in order to design the optimal blends which will allow to discriminate between different model assumptions and will show distinctive features within the experimental window. As a result, we were able to get start-up shear curves with two maxima corresponding to two molecular weights and analyze these features as a function of molecular weights and concentration.

Tuesday 4:25 Massachusetts EP27

**Rheology and mesoscale network structure of entangled polystyrene-organoclay solutions**

Jin Li1, James M. Fitz-Gerald2, and James P. Oberhauser1

1Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, United States; 2Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA 22904, United States

Many of the desirable properties of polymer-clay nanocomposite materials are believed to derive from the microstructure induced by processing. Here, we explore the rich rheological behavior of these material systems by working with entangled polystyrene-organoclay solutions, drawing analogies to both entangled polymer and dispersion rheology.

Solutions are comprised of high molecular weight, narrow molecular weight distribution polystyrene ($M_n = 8.42 \times 10^6$ g/mol), organically modified montmorillonite clay from which excess free surfactant has been removed, and $p$-xylene. The polymer concentration has been fixed relative to the amount of solvent such that the average number of entanglements per chain is approximately 10 in a pure polystyrene solution. Organoclay has been added to similarly entangled solutions at loadings of 0.89 and 2.68 wt% relative to solvent. Pure organoclay dispersions of similar loadings are studied as reference materials.
Various deformation histories, including oscillatory shear, steady shear, and step-strain, are imposed in a mechanical rheometer to examine the influence of organoclay filler on polymer relaxation dynamics. The sample with 0.89 wt% organoclay exhibits a divergent viscosity at low shear rates similar to that observed for more highly filled polymer nanocomposite melts; however, the linear viscoelastic response remains dominated by the polymer, and the Cox-Merz rule is satisfied. At 2.68 wt% organoclay loading, the rheology is dominated by organoclay, as evidenced by pronounced yield behavior, incomplete relaxation following step-strain, and failure of Cox-Merz. Yield behavior suggests the existence of a mesoscale organoclay network that is stabilized by the elasticity of the polymer. A novel wet SEM technique provides direct imaging of the inferred mesoscale organoclay network in the quiescent state. Rheological data are discussed in the context of that network and classic entangled polymer rheology.

Tuesday 4:50 Massachusetts

**Rheology of randomly branched poly-vinylidene fluoride**

Nafaa Mekhilef and Lotfi Hedhli

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The rheology of randomly branched polyvinyl fluoride (b-PVDF) was investigated in the molten state. Shear and extensional rheology showed that the resin exhibits a low frequency onset of shear thinning and strain hardening respectively. The presence of chain branching was corroborated using size exclusion chromatography coupled with MALLS as well as fluorine NMR. SEC-MALLS showed that the branched PVDF exhibits a lower radius of gyration towards the high end of the molecular weight distribution when compared to linear counterparts while NMR showed the presence of branch points that are long enough to cause the rheological effects observed.

Tuesday 5:15 Massachusetts

**Viscoelastic behavior of low molecular weight sulfonated polystyrene ionomers**

Hongying Zhao\(^1\) and R. A. Weiss\(^2\)

\(^1\)Polymer Program, University of Connecticut, Storrs, CT 06269, United States; \(^2\)Chemical Engineering, University of Connecticut, Storrs, CT 06269, United States

The rheology of sulfonated polystyrene ionomers (SPS) was characterized using a series of ionomers prepared from a low molecular weight (4,000), narrow molecular weight distribution (1.06) polystyrene. Two sulfonation levels were examined, 2.5 and 4.8 mol%, and the metal counterions was varied across the alkali metal series of the periodic table. Dynamic and steady shear experiments were performed. For SPS with 4.8% sulfonation level, good time-temperature superposition (TTS) was obtained for KSPS, RbSPS and CsSPS, while TTS for G" failed for LiSPS and NaSPS. The dynamic properties of LiSPS (4.8) showed same behavior as McLeish's H-polymers, which indicated the form of H structure within LiSPS(4.8) ionomer. All TTS for G" failed for lower sulfonation level (2.5%). The steady shear viscosity increased with sulfonation level and as the size of counterion decreased for the alkali metal salts, whereas the parent polystyrene exhibited no elasticity. Polystyrene with Molecular weight of 50,000 was also studied. It was observed that not only the normal force differences showed up at higher shear rates, but also its viscosity value was very close to that of RbSPS (2.5) ionomer. Shear thinning behavior were observed for the lower sulfonation level, while shear thickening can be observed for LiSPS2.5 and NaSPS2.5 under certain temperatures. There were no shear thinning can be observed for the higher sulfonation level ionomers. The microstructure of the SPS ionomers was also studied using small-angle X-ray scattering (SAXS). A scattering peak and an upturn in intensity near zero angle confirmed the existence of ionic clusters. A further in-situ shear SAXS test of RbSPS(2.5) showed the scattering peak intensity decreased as shear rate increased, which indicated the dissociation of ionic clusters within RbSPS(2.5) ionomer.

Tuesday 5:40 Massachusetts

**Dynamics of flexible ring polymers in obstacle environment**

Balaji Iyer\(^1\), Vinay Juvekar\(^2\), and Ashish Lele\(^3\)

\(^1\)Polymer Science and Engineering, National Chemical Laboratory, Pune, India; \(^2\)Department of Chemical Engineering, Indian Institute of Technology, Mumbai 400076, India

We present a mean field coarse grained molecular model for the dynamics of flexible ring polymers in a topologically constraining fixed obstacle environment (ring in a crosslinked gel devoid of solvent). The basis of our model lies in the similarity between the static structure of ideal flexible rings in a fixed obstacle environment and randomly branched polymers. Consequently, our model formulation is inspired by the pom-pom model in which the topological constraints are handled via the tube model framework. We obtain expressions for the centre of mass diffusion coefficient and the longest relaxation time, which agree with the scaling relations proposed earlier by Obukhov et al. [Phys. Rev. E, 1994]. Next, we extend our model to the case of melt of rings (mobile obstacles) and derive expression for the relaxation modulus. The predictions of our model are found to be in semi-quantitative agreement with frequency sweep data.
We exploit particle tracking microrheology to clarify the effect of a constant applied shear during the gelation of a Gellan Gum polymer solution in the presence of monovalent salt. The shear applied during the gelation induces a microstructure which is responsible for a clear variation of the bulk rheological properties of the system if compared with the gel prepared with no applied shear during gelation. Not only the linear elastic response has a clear dependence on the microstructure but also the critical strain and the critical stress above which the system starts to behave nonlinearly. We systematically study by conventional oscillatory rheology micro-structured Gellan Gum Hydrogel systems at different polymer and salt concentration. We study both the linear elastic response and the critical strain and stress. Surprisingly, we find that all the data can be coherently accounted for by simply considering the micro-structured fluid as composed of microgel particles whose size is set by the strength of the shear applied during the gelation, the volume fraction by the polymer concentration, and the single microgel elastic properties by the ionic strength of the system.

**Symposium MR**  
**Microrheology**

Organizers: Patrick Spicer and Victor Breedveld

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**Rheology and microrheology of microstructured gellan gum systems**  
Marco Caggioni¹, Patrick Spicer², and David Weitz³  
¹DEAS, Harvard University, Cambridge, MA 02138, United States; ²Complex Fluids Research, The Procter and Gamble Company, West Chester, OH 45609, United States  
We assume the Generalized Langevin Equation (GLE) model for thermal fluctuations of passive microbeads in a viscoelastic material. Our goal is to develop tools for direct simulation of GLEs for a known viscoelastic relaxation modulus, and to develop inverse characterization tools for the relaxation modulus from time series of microbead displacement data. We first demonstrate the concepts and tools with the standard Langevin Equation (LE) for viscous fluids, including the relationship between the exact LE solution and autoregressive time series models.

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**Dynamics of individual single-walled carbon nanotubes in water by real-time visualization**  
Nikta Fakhri¹, Dmitri A. Tsyboulski², Rajat Duggal³, R. Bruce Weisman², and Matteo Pasquali¹  
¹Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States; ²Chemistry Department, Rice University, Houston, TX, United States; ³GE plastics, Vernon, IN, United States  
Individual single-walled carbon nanotubes (SWNTs) in aqueous suspension are visualized directly by visible as well as near-infrared fluorescence videomicroscopy. The visible imaging is based on simple tagging of the SWNTs with a biocompatible fluorescent marker. The near-infrared imaging relies on the intrinsic fluorescence of semiconducting SWNTs; it provides more in-depth information for dynamical analysis. The dynamics of individual SWNTs in water are observed and quantified for the first time. We measure the confined rotational diffusion coefficient and find it in reasonable agreement with predictions based on confined diffusion of dilute Brownian rods. We determine the critical concentration at which SWNTs in suspensions start interacting. By analyzing the fluctuating shape of long SWNTs in the 4 to 8 micron range, we determine that their persistence length is in agreement with theoretical estimates. The diameter of the imaged individual SWNTs can be determined from the fluorescence spectra and the diameter dependence of bending stiffness is discussed.

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**Continuum-microscopic computation of constitutive laws for viscoelastic flow**  
Sorin M. Mitran  
Applied Mathematics, University of North Carolina, Chapel Hill, NC, United States  
A method to compute continuum viscoelastic flows starting from spatially inhomogeneous microscopic models is presented. Adaptive mesh refinement is employed on the continuum level to dynamically locate areas of high flow property gradients. Areas so identified are sampled at a microscopic level in accordance with some microscopic model (e.g. Kelvin, Zener, Burgers) which features spatially varying properties. A hierarchical microscopic simulation is carried out in order to computationally identify statistical moments entering into the continuum level constitutive law. Dynamics from a finer level of microscopic simulation are analyzed through principal orthogonal decomposition and higher-order tensor decompositions in order to identify modes that are representable on a coarser level. Thermal background is captured through a multi-level heat equation. Applications especially related to rupture phenomena are presented.

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**Autoregressive (direct) and maximum likelihood (inverse) methods for microrheology simulations and experiments**  
Lingxing Yao¹, M. Gregory Forest¹, Timothy Elston², and John Fricks³  
¹Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3250, United States; ²Pharmacology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, United States; ³Statistics, Penn State University, University Park, PA 16802, United States  
We assume the Generalized Langevin Equation (GLE) model for thermal fluctuations of passive microbeads in a viscoelastic material. Our goal is to develop tools for direct simulation of GLEs for a known viscoelastic relaxation modulus, and to develop inverse characterization tools for the relaxation modulus from time series of microbead displacement data. We first demonstrate the concepts and tools with the standard Langevin Equation (LE) for viscous fluids, including the relationship between the exact LE solution and autoregressive time series models.
Next, the connections between exact solutions and multivariate autoregressive time series models are demonstrated for a class of GLEs. Using this linear multivariate time series model, we show how, given path data of microbeads, one may calculate an exact likelihood function, thereby producing maximum likelihood estimators of parameters in the shear relaxation modulus. For microrheology, these techniques yield storage and loss moduli distributions (e.g. best fit parameter values and variance), and estimates of the best finite model approximation of the complex modulus. We also discuss a new direct simulation algorithm for GLEs using these statistical concepts.

Tuesday 3:10 Connecticut
**One– and two–particle microrheology of yield–stress fluids**
Felix K. Oppong and John de Bruyn
*Physics and Astronomy, University of Western Ontario, London, Ontario, Canada*

We have performed microrheological measurements using the multiple-particle tracking technique on two types of yield-stress fluids, namely Carbopol ETD 2050, a polymer gel of a suspension of swollen microgel particles and Laponite RD, a synthetic clay consisting of a suspension of colloidal particles. Using single-particle microrheology, we find that on the length scale of our measurements, the fluids are heterogeneous, with different particles in the same fluid sampling different microrheological environments. The degree of heterogeneity is more pronounced in Carbopol where particles sampling the same fluid can be grouped into different populations based on the degree of mobility. The microrheological viscous and elastic moduli, calculated from the autocorrelation of the probe particle positions were several orders of magnitude smaller than the corresponding bulk measurements made with a conventional shear rheometer. This confirms the fact that the particles are measuring the small-scale rheology of the material instead of the bulk. The two-particle technique, on the other hand, gives the viscoelastic parameters as a function of the distance between the particles based on the cross-correlation between particle positions and so allows us to probe the crossover from microscopic to bulk rheological parameter values. In this talk, we will compare our results from the one and two particle analysis with the bulk rheological measurements.
dynamically formed when otherwise defect-free samples flow past obstacles within the microchannel. We measure the pressure drop and defect velocity and relate these to the observed defect size and the microchannel geometry. These results indicate that microfluidics can provide a novel way of probing the nonlinear behavior of layered fluids under flow.

Tuesday 4:50 Connecticut

**The transient flow behaviour of worm-like surfactant solutions undergoing a planar extension in micro-fabricated contraction geometries**

Lucy E. Rodd and Justin J. Cooper-White

*Division of Chemical Engineering, The University of Queensland, Brisbane, QLD 4072, Australia*

The transient flow behaviour following a step-increase in flowrate is investigated in the planar entry flow of worm-like surfactant solutions flowing through a 4:1 micro-fabricated contraction geometry. Experiments are performed using a series of aqueous solutions consisting of 1 - 10 mM cetyl trimethyl ammonium bromide and equal molar quantities of sodium salicylate, over a range of flow conditions in which the effects of inertia are negligible. The long relaxation times and highly shear-rate-dependent viscosities of these fluids lead to large elastic corner vortices which extend far upstream of the contraction. Following a step-increase in flowrate, progressive changes in the upstream kinematics may be categorized according a number of flow regimes including vortex growth, vortex collapse and Newtonian-like flow. It is found that these fluids exhibit an 'induction time' prior to the onset of vortex growth. During vortex growth, vortices may grow sufficiently far upstream of the contraction to form a nearly inviscid core of fluid that is bounded by a layer of slow-moving fluid near the walls of the geometry. The evolution of the upstream kinematics leading up to and following this event is characterized using micron-particle image velocimetry, which is also used to confirm the presence of a "shear-banding" phenomenon previously observed in shearing flows of similar worm-like surfactant systems. The evolution of the upstream kinematics is also accompanied by a transient response in the differential pressure drop measured between two positions upstream and downstream of the contraction, which exhibits a maximum during periods of maximum vortex growth. Post this complex transient behaviour, all of these fluids ultimately exhibit Newtonian-like flow at steady-state conditions. This work is relevant to the design of agricultural chemical dispersion processes, which often utilize low-viscosity surfactant solutions exhibiting a worm-like micellar microstructure.

Tuesday 5:15 Connecticut

**Rheological properties of polymer melts in confined shear flow from dynamic Monte Carlo simulations**

John R. Dorgan

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

The viscoelastic properties of dense polymer melts in shear flow are examined using dynamic Monte Carlo simulation for plate spacings less than 10 times the molecular radius of gyration. The methodology employed consists of the cooperative motion algorithm of Pakula and a derived biasing technique based on previous studies of Binder and Baushnagel. For relatively large plate spacings and slow flows, a uniform linear velocity profile is obtainable. Use of the Kramers form for entropic springs allows the calculation of stress in the simulation providing a means for exploring rheological properties including viscosity and normal stress differences. Results are in excellent agreement with well-established experimental facts; a shear thinning viscosity is obtained, the first normal stress difference increases with shear rate, and the first normal stress coefficient decreases with shear rate. Evidence of entanglements are present for longer chain lengths and for fast flows, the linear velocity profile is lost and shear banding is observed. A non-monotonic stress with shear rate is found in conjunction with the shear banding and mechanistically this is attributable to a cohesive failure with an excess of chain ends being found at the slip plane. Results for variable plate spacings shed some insight into novel confinement effects that are being exploited in emerging areas of nanotechnology.

Tuesday 5:40 Connecticut

**Viscoelastic effects in a three-dimensional curved micro channel flow**

Patrick D. Anderson

*MaTe, Eindhoven University of Technology, Eindhoven, Noord Brabant 5600 MB, The Netherlands*

In this paper we show that we can drastically improve mixing by the addition of a trace amount of a polymer additive even in very simple geometries. The effect of the polymer additive, for example PEO, is that second-normal stresses are added to the system which in turn induce secondary flow, even in the absence of inertia. Here mixing in a simple periodic curved micro channel is studied in the creeping flow regime for viscoelastic liquids, see [ref{geom}] for a two-dimensional projection of the geometry; a single element of the periodic channel is shown in fig.--[ref{mesh}]. To model the flow a DEVSS-SUPG-G finite-element formulation is used including the Giesekus constitutive model which exhibits second-normal stresses. A secondary flow is observed which different topological structures at different slices. To analyse the mixing behaviour the mapping method is applied. Initially, the mixing process starts with an uniformly layered structure of black and white material, placed in the cross section, which after a number of channels is advected in to much thinner striations where diffusion can become dominant. Results are shown for the curved channel flow, but the concepts is not based on the curvedness of the channels as will be shown during the presentation to work for straight channels. In addition results are presented which distinguish the effect of inertia versus elasticity. Finally, mixing is quantified as a function of the concentration of the polymer polymer additive.
With increasing pre-shear rate and pre-shear duration. At large enough extension rate, the fluid filaments have been observed not to fail under extensional rheology and the effect of pre-shear. Pre-shear was found to delay the onset of strain hardening and the delay was found to increase progressively with increasing range of extension rates, pre-shear rates and pre-shear durations in order to acquire a better insight into the capillary thinning, but to rupture at a critical value of the elastic tensile stress. This failure has been found to be independent of the imposed pre-shear prior to the onset of stretch. Both CTAB/NaSal and CPyCl/NaSal micellar solutions of varying concentrations were tested over a progressively increasing range of extension rates, pre-shear rates and pre-shear durations in order to acquire a better insight into the extensional rheology and the effect of pre-shear. Pre-shear was found to delay the onset of strain hardening and the delay was found to increase with increasing pre-shear rate and pre-shear duration. At large enough extension rate, the fluid filaments have been observed not to fail under capillary thinning, but to rupture at a critical value of the elastic tensile stress. This failure has been found to be independent of the imposed extension rate, but a strong function of the pre-shear. Flow induced birefringence measured simultaneously with the stress, have been used to analyze the local anisotropy in the molecular conformation of the wormlike micelles. Finally, an attempt is made to correlate the variation in the finite extensibility parameter between micellar entanglement points in the chain, with increase in the uniaxial extension rate in order to demonstrate the morphological changes induced by strong shear and extensional flows on wormlike micelle solutions.

With the increasing application of wormlike micelles as rheological modifiers in many consumer products, the predictions of the behavior of these solutions have become increasingly important in the recent years. A complete understanding of the fluid behavior requires the knowledge of both the shear and extensional rheology of the wormlike micellar solutions. In this talk, we present the results of our experimental measurements of the transient uniaxial extensional viscosity of a series of wormlike micelle solutions, both with and without the application of a known pre-shear prior to the onset of stretch. Both CTAB/NaSal and CPyCl/NaSal micellar solutions of varying concentrations were tested over a progressively increasing range of extension rates, pre-shear rates and pre-shear durations in order to acquire a better insight into the extensional rheology and the effect of pre-shear. Pre-shear was found to delay the onset of strain hardening and the delay was found to increase with increasing pre-shear rate and pre-shear duration. At large enough extension rate, the fluid filaments have been observed not to fail under capillary thinning, but to rupture at a critical value of the elastic tensile stress. This failure has been found to be independent of the imposed extension rate, but a strong function of the pre-shear. Flow induced birefringence measured simultaneously with the stress, have been used to analyze the local anisotropy in the molecular conformation of the wormlike micelles. Finally, an attempt is made to correlate the variation in the finite extensibility parameter between micellar entanglement points in the chain, with increase in the uniaxial extension rate in order to demonstrate the morphological changes induced by strong shear and extensional flows on wormlike micelle solutions.

Many complex fluids, such as wormlike micelles or lamellar surfactant solutions, form "shear bands" or macroscopic regions of different apparent viscosity and microstructure, when subjected to strong shear flow. In previous work relatively little attention has been paid to the role of boundary conditions in this phenomena. In this talk we explore the role of different boundary conditions for several models of complex fluids (e.g. the Johnson-Segalman model, the Rolie-Poly model for polymer solutions, and the Bautista/Manero for wormlike micelles) in planar and cylindrical Couette geometries. The boundary conditions do not affect the flow curve in the limit of small stress diffusion, but do alter the position of the bands, particularly in the planar geometry; we study the basins of attraction of different competing metastable band configurations for the different geometries. This may be important in understanding hysteresis, and for understanding experiments such as those in wormlike micelles in which three bands were seen in cone and plate geometry, with the low viscosity band in the centre.

Motivated by the collaborative development of new constitutive models, experiments have been performed on the phenomenon of shear-banding in surfactant solutions. These aqueous surfactant systems are widely used for their properties; however, many aspects of their more complex behavior are still not fully understood. A large Couette shear cell was specially designed and constructed to allow optical access in a simple shear flow of the surfactant system comprised of cationic cetylpyridinium chloride (CPyCl) with a counter-ion from sodium salicylate (NaSal) in a constant 2:1 molar ratio, in brine (NaCl). Above a critical stress, this well-studied system is known to enter a non-linear regime in which there is a plateau in the stress. Within this plateau, the fluid is observed to form distinct bands of varying shear-rate. By measuring velocity...
profiles using particle-image velocimetry (PIV) and stress-fields with a pointwise polarimetry flow-induced birefringence (FIB) method, in both steady and transient startup flows, we will be able to make conclusions about the mechanism and development of the banded structure. Our experiments focus on obtaining high spatial and temporal resolution PIV and FIB results, to provide insight on this flow behavior, as well as provide a full set of experimental data with which to drive development of constitutive models to predict shear-banding and subsequently compare to theoretical results.

Tuesday 3:10 Rhode Island

A numerical study of dilute wormlike micellar solutions in Taylor-Couette flow

Louis F. Rossi
Department of Mathematical Sciences, University of Delaware, Newark, DE 19716, United States

We present a numerical study of dilute worm-like micellar solutions in Taylor-Couette flows. Worm-like micelles are long cylindrical structures composed of amphiphilic surfactant molecules which self-assemble in solution. These structures interact with one another forming entangled networks similar to polymers, but they can break and reform on different time scales. To gain a fundamental understanding of their rheology, worm-like micelles have been the subject of many distinct experimental, theoretical and numerical studies. This project is an attempt to reconcile recent theoretical, experimental and numerical findings. In this project, we use a new self-consistent model for semi-dilute micellar solutions (Cook Rossi 2004) based on bead-spring dumbbells. Overlap, entanglement and the continuous breaking and reforming of the wormlike micelles in the semi-dilute regime are modeled by the non-affine deformation of the microstructure. The model arises using kinetic theory assuming that the viscoelastic characteristics of the semi-dilute solution properties could be lumped into a bead-spring mechanism, resulting in a system that couples stress and micelle number density. Solutions to this nonlinear system can be computed using high order polynomial collocation. We explore parameter space using a variety of collocation methods. Recent numerical investigations demonstrate that this model produces a pronounced plateau in the stress-strain rate flow curve. While numerical results have shown excellent qualitative agreement with detailed velocity profiles measured in laboratory experiments by Rothstein and Miller (and also Hu and Lips 2005), this project explores direct quantitative comparisons with experimental measurement. The key issues are the selection of stress boundary conditions and the model parameter controlling bead-spring slippage or tumbling.

Symposium VS
Viscoelasticity of Solids, Thixotropy and Glasses

Organizers: Jan Mewis and Gregory McKenna

Tuesday 4:00 Rhode Island

Microscopic theory of the nonlinear dynamical properties of polymer glasses

Kang Chen and Kenneth Schweizer
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A statistical mechanical theory of collective dynamic barriers, slow segmental relaxation and the glass transition of deeply supercooled polymer melts has been recently developed by combining and extending methods of mode coupling, density functional and activated hopping transport theories [1,2]. The melt is treated as a liquid of statistical segments, and the theory is built on the idea that collective density fluctuations on length scales longer than the local cage scale control the glassy dynamics. For long chains the segmental relaxation time is a function of a single thermodynamic state and material dependent dimensionless parameter which is specified by the amplitude of thermal density fluctuations (compressibility) and a segmental density. This theory has now been generalized to treat nonlinear mechanical properties below the glass transition temperature. External deformation modifies the nonequilibrium free energy that controls glassy segmental motion in a manner which accelerates viscous flow and softens the elastic shear modulus. Mechanical response is studied in step strain, constant strain rate, and constant stress modes. Calculations of stress-strain curves and yield points have been performed, and their (generally strong) dependence on temperature and strain rate established. Deformation induced reduction of the alpha relaxation time has also been studied, and yielding is found to correspond to a nearly universal connection between the barrier hopping time and strain rate. Comparisons of the theoretical results with experiments on polystyrene, PMMA and polycarbonate glasses have been performed. Generalization of the theory to treat large deformation induced distortion of chains, which is relevant to the ubiquitous and poorly understood strain hardening behavior, is possible. [1] K.S.Schweizer and E.J.Saltzman, J.Chem.Phys., 121, 1184 and 2001 (2004). [2] K.S.Schweizer, J.Chem.Phys., 123, 224501 (2005).

Tuesday 4:25 Rhode Island

Ubiquity of soft glassy dynamics in polypropylene-clay nanocomposites

Mark A. Treece and James P. Oberhauser
Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, United States

Polymer-clay nanocomposites (PCNs) exhibit rich rheological behavior, including significant time-dependence over exceptionally long time scales. Furthermore, the relaxation of flow-induced clay orientation has been shown to be non-Brownian and perhaps influenced by attractive interactions between organoclay domains.

Central to the discussion of organoclay disorientation kinetics and relaxation in PCNs is the analogy to the dynamics of soft colloidal glasses. Glassy colloidal suspensions have mechanical properties similar to metastable soft solids, properties that may evolve continuously over time in a
way characteristic of systems far from equilibrium and associated with the metastable, heterogeneous structure of soft materials on mesoscopic length scales. Particle motion is described by a cage-diffusion process. Small excursions within the "cage" formed by neighboring particles occur on fast time scales, while rearrangement of the cages themselves, tantamount to particles escaping from their cages, occurs over increasingly long time scales. During this slow "gelation" process, particles may form clusters that eventually collect into a percolated network. The imposition of a deformation in excess of the yield stress, however, is postulated to rejuvenate the energy landscape, analogously to increasing the temperature above the glass transition.

Melt-blended PCNs are inherently out-of-equilibrium, having experienced intense shearing and subsequent rapid cooling. Here, we focus upon a series of melt-blended polypropylene-clay nanocomposites whose rheology bears the logarithmic time dependence characteristic of glassy systems, irrespective of clay concentration, exfoliation, dispersion, and compatibilization. Both small-amplitude oscillatory shear, steady shear, and a combination of the two are employed in order to contrast the transient rheology of unsheared (i.e., as-processed) and sheared (i.e., flow-aligned) samples and the influence of time, thermal, and deformation history.

Tuesday 4:50 Rhode Island

**Aging and solid or liquid behavior in pastes**

Philipppe Coussot1, Guillaume Ovarlez2, and Xavier Chateau3

1LMSGC, LCPC-CNRS, Champs, France; 2Laboratoire des Matériaux et Structures du Génie Civil, CNRS-LCPC, Champs sur Marne, France; 3LMSGC, Navier Institute, Champs sur Marne 77420, France

We carried out systematic creep tests after different times of rest and over sufficiently long times with pasty materials of various internal structures in a Couette geometry. From an analysis of the data taking into account the inertia of the system and the heterogeneous distribution of stress, we show that: (i) for a stress below the yield stress these materials remain solid but undergo residual, irreversible deformations over long time which exhibit some trends typical of aging in glassy systems; (ii) as a result of thixotropy (or aging) in the solid regime the elastic modulus increases logarithmically with the time of rest; (iii) in the liquid regime the effective behavior of the material can be well represented by a truncated power-law model, (iv) a fundamental parameter of the solid-liquid transition is a critical shear rate (associated with the yield stress) below which the material cannot flow steadily.

Tuesday 5:15 Rhode Island

**Nonlinear rheology and ageing of soft colloidal glasses**

George Petekidis and Dimitris Vlassopoulos

IESL-FORTH, Heraklion, Greece

A competition of intrinsic slow dynamics with shear-induced rearrangements is observed in a wide range of soft glassy materials. Here we present experimental evidence of the effects slow dynamics have on the rheology (and vice versa) of model systems with hard and soft interparticle potential. The two systems discussed are a) high volume fractions of sterically stabilized hard sphere colloids and b) concentrated solutions of soft multiarm star polymers in an athermal solvent. In both samples the linear viscoelastic properties evolve with waiting time after a shear induced rejuvenation revealing a progressive stiffening of the vitrified state. Using creep experiments we investigate the way such states respond under stresses, below and above the yield stress and how such behavior is affected by the age of the sample. For stresses below the yield stress a constant strain plateau is reached at long times; its specific values depend both on stress and waiting time. Furthermore, the elastic recovery of such colloidal glasses related with the so-called "cage elasticity", the relaxation of the stress-induced distorted particle environment when the stress is removed is monitored in both systems as a function of volume fraction and waiting time. Finally, the role of particle interactions is discussed by comparing the results from the two systems.

Tuesday 5:40 Rhode Island

**Linear viscoelasticity and non-linear transitions in a soft colloidal glass of star polymers**

Matthew E. Helgeson1, Norman J. Wagner1, and Dimitris Vlassopoulos2

1University of Delaware, Newark, DE 19716, United States; 2I.E.S.L., F.O.R.T.H., Heraklio, Greece

Soft colloidal particles at sufficient particle density undergo a transition to a kinetically arrested state, similar to the glass transition in hard spheres. Star polymers, due to their tunable size and functionality, serve as model particles by which to study glassy dynamics of soft colloidal suspensions. This work explores the use of rheological measurements as a tool to probe the equilibrium structure and the transition to flow in glassy suspensions of monodisperse, high functionality star polymers in an athermal solvent above the glass transition. Combining oscillatory shear and stress relaxation measurements allows for the characterization of the viscoelastic moduli over eight orders of magnitude in oscillatory frequency, yielding long-time relaxation behavior previously unreported for such systems. The linear viscoelasticity of the star polymer glass is described well at moderate frequencies by Mode Coupling Theory (MCT) predictions using model parameters for hard spheres, indicating similarities in the relaxation processes of hard and soft colloidal glasses. However, the non-linear behavior of the star glass contains behavior previously unreported for hard sphere systems. Specifically, the critical strain amplitude for shear melting follows a systematic, rate-dependent trend. Additionally, a secondary maximum in the loss modulus after the onset of shear melting is observed at both low and high frequencies, which is annealed out upon complete fluidization of the star polymer suspension. The overall non-linear behavior of the star polymer glass is discussed in terms of two phenomenological mechanisms: (i) deformation and yielding of the cage-like glassy microstructure, and (ii) disentanglement of overlapping stars. Finally, the influence of phenomena such as thixotropy and slip on rheological measurements of the star glass will be discussed, leading to more complete understanding of the processes leading to flow in soft colloidal glasses.
Rheological tests and process model for frothed carpet compounds

Nick Triantafillopoulos, Bruce Schreiner, and Douglas W. Bousfield

Rheology of three-phase (solid-liquid-air) foams is of interest in industrial application processes, such as the roll applicator in the production of tufted carpets. The foamed compound is the adhesive that holds the fibers in place. The correct penetration of this compound into the web is important to obtain good product quality and end-use properties. Two rheological tests are proposed that characterize the rheology of this type of foam in a manner that is related to the application process. One test involves a rapid ramping of the shear rate up to a target and then back down to obtain the shear-thinning nature of the compound. The other test involves applying a shear stress pulse (step) for a very short period of time and then letting the foamed relax while measuring strain. A model is developed to predict the penetration of the foam into the web during the application. The model links the process parameters, such as web speed, applicator roll gap, and roll diameters to the compound rheology and penetration. The model uses the shear-thinning, thixotropic nature of these compounds to predict the pressure pulse in the roll application and the penetration into the web. The results for two compounds are compared. These compounds are similar in many ways, but have quite different rheological responses to the shear rate ramp test. One compound is known empirically to "penetrate" (into the web) more than the other. The rheological tests show that this compound has (a) a steeper shear-thinning curve, and (b) more strain under stress than the "non-penetrating" compound. The model predicts the correct trend that is seen in practical application, verifying that the relevant physics and rheology are correctly incorporated. Furthermore, the rheological behavior of frothed compounds reflects the size of the induced air bubbles and therefore the stability of the foam.

Rheogical behavior of microbubble suspension in food application

Yuyi Shen, Marjorie L. Longo, and Robert L. Powell

Microbubbles are micron-scale hollow spheres (normally 10-200 um) with a gaseous core coated with a thin shell. Potentially, a monodisperse population of such bubbles could be introduced as part of the processing of a food. Monodisperse microbubble suspension was generated using flow focusing technique. Using this technique, we are able to control microbubble size with different flow rate ratio of air and emulsifier solution, and it lead to the ability to control the air fraction of fluids. The air entrainment and stability of this multiphase and multicomponent system are studied. Based on the fact that the microbubbles are very stable for a short time period, a rotational rheometer is used to measure the relationship of "real time" bubble suspension rheological properties. A semi-empirical approach is used analyze the rheological behavior of this monodisperse microbubble suspension. It was revealed in the paper that the microbubble suspension shows power law rheology at low shear rate (up to 20 1/s). The viscosity of the fluids is related directly with the air fraction. Oscillation rheological results also disclose the viscoelasticity of the fluids. A food grade emulsifier (mixture of monoglyceride, diglycerdie and sodium stearoyl lactylate) as well as PEG -40 was used as an alternative of pure saturated phospholipids to form the thin shell. A fluorescence microscopy technique is used to study the microstructure and dissolution behavior of these microbubbles in degassed media. Furthermore, we studied concurrently the domain features and the surface pressure-area isotherm of this emulsifier in a Langumir monolayer.

Connecting linear to non-linear rheology of wheat flour doughs

Trevor S. Ng and Gareth H. McKinley

The strongly nonlinear rheological properties of dough arise from the interactions of a highly entangled polymeric matrix and a high filler concentration of hydrated and charged starch particles. When starch separated from the flour is mixed with water, a discontinuously-shear thickening fluid is formed, much like that formed from corn starch. The addition of a small amount of gluten (a high molecular weight branched polymer) imparts the strong viscoelastic nature commonly associated with a strong wheat flour dough. We seek to understand the mechanisms behind this dramatic change in behavior. We begin with an overview of linear and non-linear rheometric techniques that are suitable for characterizing dough in both transient shear and extension. Based on the critical-gel-like behavior often seen in doughs, we outline a rheologically consistent method to extend the properties measured in linear viscoelastic experiments to large-amplitude and non-linear deformations. We also investigate the compositional dependence of dough rheology and demonstrate a water content-modulus superposition principle and the presence of rheological aging. By combining these observations we show that the constitutive response can, to a good approximation, be factorized into terms that capture the linear relaxation modulus of the dough, a power-law dependence on deformation rate, a nonlinear strain-softening contribution, plus universal functions that describe the compositional variation and aging history.
The rheological properties of several different types of mozzarella cheese are determined by using a parallel plate, a sliding plate, an extensional and capillary rheometers over a temperature range from 25°C to 60°C. A full analysis on the experimental data is performed to obtain the true rheological properties of the cheese. Slip effects are also examined. Differences in the rheological data obtained between different rheometers are explained in a consistent and scientific manner. It is found that in general the structure of mozzarella cheese is very sensitive to temperature as loss of moisture and phase separation of its constituents greatly influence its rheology. Moreover, it is found that mozzarella cheese behaves as a viscoelastic semisolid at room temperature exhibiting evidence of a yield stress and as a viscoelastic melt at higher temperatures i.e. at 50-60°C. Finally, the processing of mozzarella cheese is assessed by means of capillary extrusion and roll forming and these results are correlated with rheological properties.

The use of intrinsic viscosity measurements to investigate molecular volume and surfactant interactions in heavy oils

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Readily accessible reserves of light crude oil are declining and attention is being focused on the extraction and upgrading of viscous tar sands, bitumens and heavy oils. The primary, commercially useful constituents of these oils are paraffins, aromatics and resins. Aromatics include asphaltenes and napthenes. In naturally occurring formations these oils are produced with up to 80% solids (sand) and formation (salt) water; inevitably during the production process emulsions are formed, the emulsifier being provided from the surface active components of the oil. Relatively, very little is known about the chemical structure of these emulsifiers with, as a consequence, little detailed understanding of the mechanisms involved in emulsion formation and emulsion breakdown. Dilute solution viscometry is a powerful tool that provides information about molecular volume (intrinsic viscosity) and therefore, under suitable conditions, molecular weight. In this paper we show that the apparently high viscosity of the crude oils is no more than that expected from the concentration dependence of viscosity. Analogous to the polymer solution situation in which an abrupt change in slope is observed at the coil overlap concentration a similar situation is demonstrated for bitumens and heavy oils (which contain large fractions of "platelet" shaped molecules containing about 25 benzene equivalents) were overlap occurs at the "excluded volume" overlap. Differences between "good" and "bad" de-emulsifiers in field situations have their origin in promoting (or not) intermolecular interactions between the surface active components of the oil leading to observable changes in intrinsic viscosity.

On tensile testing of concentrated suspensions

Andreas N. Alexandrou1, Alexander V. Bazilevsky2, Vladimir M. Entov2, K Isaev3, and Alexey N. Rozhkov2
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Rheology of suspensions and slurries is usually studied in shear - dominated experiments, while many applications involve also elongational flow, and need data related to extension. This talk describes an approach which can be used to test mobile slurries, including such as semi-solid metals (SSM) at elevated temperature, in extension. It is based on the monitoring of evolution of the shape of a liquid bridge between two disks after they were pulled apart. The approach is basically a modification of the Liquid Filament Microrheometer developed primarily for testing polymer solutions. Model sand/glycerine suspensions of different solid fraction prepared with two different particle sizes were used in experiments. Steady-state shear properties of the suspensions were determined using Couette rheometer and were approximated with the Bingham model. Then the bridge necking was monitored optically, and the data were processed using the theory of inertialless uniform thinning of a liquid column squeezed by lateral capillary pressure. Linear decrease of the neck radius in time implies effectively Newtonian behavior of the suspensions under experimental conditions. The effective viscosity derived from these data prove to be well correlated with the shear viscosity at high shear rates over entire range of concentrations studied. However, this effective viscosity is approximately twice as large as shear viscosity, and this discrepancy exists even for a Newtonian fluid (glycerol). Additional experiments with glycerol and modeling in the framework of one-dimensional theory suggest that the effective stress driving neck thinning is less than total capillary pressure in the neck, so that the effective viscosity derived from tensile experiments should be modified by the corresponding factor. A parametric study of the bridge shape evolution for nonlinearly-viscous non-Newtonian fluid was performed using an in-house 1D simulator of the bridge dynamics.
Tuesday  4:25  Cumberland/Kennebec  
**Effects of process conditions on dynamics and stability in 2-D film casting process**

Hyun Wook Jung¹, Dong Myeong Shin¹, Jang Ho Yun¹, Joo Sung Lee², and Jae Chun Hyun¹

¹Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea; ²Chemical Engineering, University of California, Berkeley, San Francisco, CA, United States

Dynamics and stability in 2-D film casting system have been theoretically investigated using Phan-Thien and Tanner fluid model. Both steady and transient solutions of this system have been successfully obtained using numerical schemes by Kim et al., JNNFM (2005). Effects of various process conditions such as aspect ratio, drawdown ratio, viscoelasticity, cooling, etc. on dynamics and instability modes, e.g., edge beads, neck-in, and draw resonance, of film casting have been systematically examined. It has been confirmed from the results of linear and nonlinear stability analyses that 2-D model is superior to 1-D film width model previously developed by our group in predicting the film casting system.

Tuesday  4:50  Cumberland/Kennebec  
**Biomodal and broad molecular weight distribution polypropylene and its effect on rheology and physical properties**

Stanley P. Westphal

Westphal Beachside Consultants, Inc., Satellite Beach, FL 32937, United States

Metallocene isotactic polyproplyenes yield a significantly lower Flexural Modulus than ZN catalyzed polypropylene's. This project was undertaken because of differences in physical properties of the resins, The Molecular Weight Distribution (MWD) of polypropylene was altered by solution blending of 2 very different molecular weight polymers. Ultra-high and Ultra-low MW species were solution blended with normal MWD polymers in decalin at a temperature of 160C. To prevent molecular segregation the hot solution was discharged into hexane. Materials were then stabilized, compression molded, cut into pellet sized pieces and then injection molded into ASTM test specimens. All of the test specimens were very broad MWD polymers. One of the effects of this was to reduce the high shear viscosity. The Spiral Flow on those resins with the high Mw tail increased 5 -12.7cm. The materials with the low Mw tail increased 25.4 - 33 cm. Melt elasticity increased when the high molecular weight tail was increased. The low shear viscosity and Mw increased for all of the blends. This gave the materials better melt strength. The blends with a low MWD tail yielded an increased Flexural Modulus of 10%. In a larger scale study the Flexural Modulus increased 30 %. With an in line, multi-reactor, polymerization process one can readily tailor product properties and performance.

Tuesday  5:15  Cumberland/Kennebec  
**Solid state viscometers for industrial process control and asset management.**

Jeffrey C. Andle

BiODE, Inc., Westbrook, ME 04092, United States

Integration of real time rheometry into industrial processes has been a long standing goal that has met with only partial success. The requirement has previously been met by ruggedizing traditional mechanical devices to allow them to withstand insertion into the process. This has led to only limited successes and the use of sampling with laboratory analysis is still prevalent. Researchers in Academia, government labs and industry have been working towards realization of solid state sensors that are capable of withstanding the process conditions without interfering with the process. This presentation will discuss the strengths and weaknesses of a family of viscometers based on piezoelectric devices. A high frequency (160 MHz), high-shear (10⁴ - 10⁷ s⁻¹) version and a moderate frequency (5.3 MHz), moderate shear rate (~10⁵ s⁻¹) version of the technology will be compared. Device physics will be discussed relative to shear rate, Maxwellian effects, particle size effects, and units of measure. Data on real fluids will be presented indicating these strengths and limitations. The relationship between frequency, shear rate, and vibration immunity will be explored and general discussions on the lower limit of frequency and shear rate for this method will be discussed relative to process conditions. Future directions of the technology to high temperatures, high pressures, and controlled/variable shear rate will be discussed. Connectivity options including CAN, Profibus, and USB will be discussed.

Finally, prototypes of a potential mass-market oil condition sensor will be discussed. This distillation of the technology is expected to enable large vehicle (buses, trucks, etc.) and critical assets (shipboard, electrical generation) lubricant condition monitoring with manufacturing volumes on the order of 1M pieces per year.

Tuesday  5:40  Cumberland/Kennebec  
**Case studies in practical, applied rheometry**

David J. Moonay

Brookfield Engineering Labs., Inc., Middleboro, MA 02346, United States

Various industrial processes require different methods for determining the viscosity and gaining insight into the rheology of highly complex, non-Newtonian, commercial products. Rheological analogies exist between products in completely different industries. Additionally, meaningful measurements must be made often in non-ideal conditions, in manners easily understandable by laymen - the operators. This presentation will discuss various case studies - including the rheological challenges and effective, practical methods for obtaining the data. Experimental artifacts will be discussed, as well. For example, a 49 wt.% mixture of Corn Starch powder in tap water was tested with a Brookfield RVDV-H+ rheometer at 21-22 °C. Freshly prepared, and tested with V-72 vane spindle from 50-250 rpm, the material was reproducibly shear-thickening with apparent viscosity increasing from approximately 120 to 360 cP. However, aged two days and then tested
with LV-2CYL cylindrical spindle at 20 rpm, the material appeared to "yield" - the viscosity peaked at 9300 cP and rapidly fell to 1600 cP by 50 s. Such behavior may be expected for this material and long-known by experienced practitioners. However, new generations of operators continually require education concerning the materials they work with, in simple terms. This is particularly important because it directly impacts product processing and, therefore, the company's economic bottom line.
Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Vermont

Do you speak thermodynamics?
Hans Christian Öttinger
Department of Materials, ETH Zürich, Zürich, ZH CH-8093, Switzerland

Thermodynamics is a simple language to formulate and analyze complex problems. In particular, nonequilibrium thermodynamics is the appropriate language to model the rheological behavior of complex fluids. The “grammar” of thermodynamics includes strong formulations of time-structure invariance, reversible-irreversible separation, Onsager-Casimir symmetry and the famous second law of thermodynamics. As for any language, fluent articulateness becomes more and more important when problems of increasing complexity or even philosophical depth are to be discussed. To illustrate the immense usefulness and potential of thermodynamics in discussing deep problems in rheology, we consider (i) systematic coarse-graining techniques based on statistical nonequilibrium thermodynamics and (ii) the role of boundary conditions (“boundary thermodynamics”). It is shown that thermodynamics provides the key to multiscale modeling and simulation as well as to formulating boundary conditions by physical rather than mathematical considerations.

Symposium BE
Blends, Emulsions and Multiphase Flows

Wednesday 9:45 Vermont

Large scale simulations of concentrated suspensions of elastic spheres: Ordering, shear thickening and jamming
Kenneth F. Higa and Jonathan L. Higdon
Chemical and Biomolecular Engineering, University of Illinois, Urbana, IL 61801, United States

Large scale hydrodynamic simulations are presented for the rheology of sheared suspensions of elastic spheres. Suspensions dynamics are studied for constant shear rate and constant stress. For dilute to moderately concentrated conditions up to volume fraction $\phi = .50$, the particles remain disordered and suspension behavior resembles hard sphere suspensions. At higher volume fractions in the range $0.50 < \phi < 0.60$, the suspensions may undergo a disorder-order transition with hexagonal packing patterns. Three dimensional probability distributions $g(x, y, z)$ are presented to characterize the suspension microstructure, while simulation videos are shown to illustrate the dynamics of structure evolution. The phase boundary is a function of the volume fraction, dimensionless elastic modulus and the strength of lubrication forces as characterized by a minimum effective separation gap $\delta_{\text{min}}$ for hydrodynamic force calculation. The calculation of the effective lubrication strength requires solution of a time dependent differential equation for the coupled elastic deformation-viscous film drainage equations for each particle contact. Constant shear rate simulations show large fluctuations in instantaneous viscosity at high volume fractions, $\phi > .50$.

Elastic spheres present a useful model system for investigating the approach to discontinuous shear thickening and jamming phenomena in concentrated suspensions. While direct simulation of hard sphere suspensions above $\phi = .50$ is difficult, the use of elastic spheres with increasingly large elastic modulus provides a useful model system to study hydroclusters and the discontinuous shear thickening regime at large $\phi$. These systems also represent an interesting intermediate regime between rigid hard spheres and concentrated suspensions of deformable droplets.

Wednesday 10:10 Vermont

Optimization of polypropylene/polystyrene/clay blend nanocomposites: An on-line morphological and rheological study
Joao M. Maia$^1$, Saehan Cho$^2$, Kyung Hyun Han$^2$, Ana V. Machado$^1$, and Jose A. Covas$^1$
$^1$Department of Polymer Engineering, University of Minho, Guimaraes, Portugal; $^2$School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea

In order to overcome the problems associated with finding an appropriate compatibilizer in polymer blends, functionalized modifier or a copolymer has usually been added to the mixture as compatibilizers. However, these are often not easily prepared and their substitution by another efficient phase mixing agent would be highly desirable. The possibility of compatibilizing incompatible polymer blends by adding
relatively cheap organoclays is very appealing from the standpoint of practical applications. In this study, morphological and rheological evolution of polypropylene (PP)/polystyrene (PS) blend clay nanocomposites were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and on-line rheological techniques. Organoclays located at the interface resulted in the dramatic reduction of particle size and narrower particle size distribution of the dispersed phase, morphological stabilization, and the increase of rheological properties. The kinetics for the compatibilization of PP/PS blend nanocomposites is also discussed based on the TEM results of the hybrids depending on melt-mixing time and in terms of the evolution of the morphology and of the rheological properties of the blends along the length of the extruder, for which purpose specific sample collecting devices on-line rheometry techniques were used. Thus, the overall aim of this work is to gain an insight into the kinetics of the compatibilisation inside the extruder, with a view to posterior optimization of the properties of the blends via the on-line tailoring of their morphological and rheological properties. In particular, attention will be paid to the influence of both processing conditions, e.g., output, temperature and screw speed and material characteristics, e.g., viscosity ratio, clay content and relative PP/PS ratios.

Wednesday 10:35 Vermont

Negative normal stresses in polymer nanocomposites
Bani H. Cipriano¹, Gary T. Cheng¹, Takashi Kashiwagi², Jack F. Dougals³, and Srinivasa R. Raghavan¹
¹Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States; ²BFRL, NIST, Gaithersburg, MD 20879, United States; ³Polymers Division, NIST, Gaithersburg, MD 20879, United States

Polymer nanocomposites containing multi-walled carbon nanotubes (MWNTs) have been reported to show the remarkable property of negative normal stresses in their melt rheology (Kharchenko et al., Nature Materials, 2004). In this study, we investigate in detail the occurrence of negative normal stresses in polystyrene/MWNT nanocomposites prepared by melt-compounding. Consistent with earlier findings, we observe negative normal stresses in samples with high MWNT loadings, where a jammed network of nanotubes is present. However, we find that the normal stresses are very sensitive to the flow history and show unusual trends in transient rheological experiments. Moreover, the sign and magnitude of the normal stresses are also influenced by sample annealing at elevated temperatures. To determine whether negative normal stresses are ubiquitous in jammed particle networks, we also study the melt rheology of polystyrene/organoclay nanocomposites at high organoclay loadings. Taken together, the results will be used to construct a physical picture detailing the origin of negative normal stresses in these polymeric materials.

Wednesday 11:00 Vermont

Deformation, orientation, and alignment during shear and elongation of a polycarbonate/carbon nanotubes composite in the melt
Ulrich A. Handge¹ and Petra Pötschke²
¹Institute of Polymers, Department of Materials, ETH Zurich, Zurich 8093, Switzerland; ²Leibniz Institute of Polymer Research Dresden, Dresden 01069, Germany

In order to create polymeric materials with enhanced properties, commercial polymers are filled with carbon nanotubes. In this study, we investigated the rheological properties of a polycarbonate/carbon nanotubes (2.0 wt.% composite in shear and melt elongation. The objective of our study was to elucidate the influence of the carbon nanotubes network on the rheological properties. Our experimental results revealed that the influence of carbon nanotubes was large if the externally applied stress was small. Therefore the storage and the loss modulus in the low frequency range of the harmonic shear oscillations strongly exceeded the corresponding values of pure polycarbonate. In melt elongation, the addition of 2.0 wt.% carbon nanotubes only moderately changed the transient elongational viscosity. However, in recovery the transient recovered stretch of the composite was much smaller than the corresponding values of pure polycarbonate. This effect was explained by the reduced stretch of the macromolecules during elongation of the composite and the yield stress which was caused by the arrangement of carbon nanotubes.

Wednesday 11:25 Vermont

Rheological properties of short fiber filled polypropylene in extensional flow
Julien Férec¹, Jose Roberto R. Siffert², Marie-Claude Heuzey², Pierre J. Carreau¹, and Gilles Ausias³
¹Center for Applied Research on Polymers and Composites, Montréal, Québec H3C 3A7, Canada; ²Pontificia Universidad Católica-RJ, Rio de Janeiro, Brazil; ³Laboratoire de Génie Mécanique et Matériaux, Lorient, France

The behavior of short glass fibers - polypropylene suspensions in extensional flow was investigated using the SER wind-up drums geometry (Extensional Rheology System) with a strain-controlled rotational rheometer. The filled polypropylenes contained respectively 10, 20 and 30 wt.% of short glass fibers. Special care was devoted to sample preparation in order to control initial fiber layout in two configurations, i.e. orthotropic (or random in plane) and fully aligned. In the latter case, several experiments were achieved with fibers aligned in the flow direction and perpendicular to it. Effect of fiber initial orientation and concentration on tensile start-up flow was examined. The suspensions tensile stress growth coefficient normalized by that of the matrix showed a transient behavior at low Hencky strain followed by a constant value at higher strain. This behavior was attributed to the fiber rearrangement. The impact of particle shape factor was also investigated by comparing the elongational properties of the fiber-filled samples with those of glass bead-filled polypropylene. Finally, the measured transient elongational stress growth data were compared with the predictions of the Folgar-Tucker-Lipscomb model. For this model, errors due to the use of closure approximations were avoided by a numerical resolution of the fiber distribution function used to calculate the high order orientation tensors.
Symposium PS
Polymer Solution Rheology: Molecular-scale Modeling and Experiments
Organizers: Ron Larson and Jimmy Feng

Wednesday 9:45 Massachusetts
Experimental assessment of the Zimm model for dilute polymer solutions
Timothy P. Lodge
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States
Fifty years have elapsed since Bruno Zimm published his landmark paper on the bead-spring model for dilute solutions of flexible chains with intramolecular hydrodynamic interactions. An extensive experimental program, conducted primarily by John Ferry and his "academic descendants", has shown the theory to be quantitatively correct in its intended domain of validity, i.e., for the chain dynamics of high molecular weight polymers at infinite dilution in a theta solvent. The effects of excluded volume have been incorporated successfully in a variety of ways, which usually involve a trade-off between simplicity and rigor. This approach has also been extended to cover branched homopolymers of different architectures, and block copolymers. On the other hand, chain dynamics measurements at moderate molecular weight, and at high effective frequencies, have shown rather interesting departures from expectation. These results suggest, among other things, that the solvating medium is significantly affected by the presence of the polymer, and that fundamental "bead-spring" unit may be remarkably large.

Wednesday 10:35 Massachusetts
Linear viscoelasticity of semidilute polymer solutions
Ralph H. Colby
Materials Science and Engineering, Penn State University, University Park, PA 16803, United States
The scaling approach to describe the viscosity, relaxation time, diffusion coefficient and terminal modulus of semidilute solutions of neutral polymers in good solvent and theta solvent, and polyelectrolyte solutions, will be reviewed and compared with experimental data. The essential idea (due to de Gennes) is a correlation length that separates the small scales where excluded volume and hydrodynamic interaction are important, from the large scales where both are screened. High frequency response, probed mainly by Ferry and Schrag, identifies the viscoelastic mode structure, with a crossover from Zimm-dynamics at high frequencies (within the correlation length) to Rouse dynamics at lower frequencies and larger spatial scales.

Wednesday 11:00 Massachusetts
Testing universal scaling of rheological properties in semi-dilute polymer solutions
Youngsuk Heo and Ronald G. Larson
Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States
Numerous models and theories have been developed to successfully explain rheological behavior of well-entangled polymer melts and solutions in both linear and non-linear regimes. However, solutions at polymer volume fractions slightly or modestly above the overlap concentration in the semi-dilute regime are not as well understood due to the inadequacy of the tube model in this weakly entangled regime. The "blob" theory was proposed to describe how in the semi-dilute regime excluded volume interactions are screened at distances larger than the blob size. Thus, each blob is a rescaled monomer representing a portion of the polymer chain plus the solvent in its vicinity, and the solution then is equivalent to a dense melt of chains of blobs. While not giving explicit formulas for viscoelastic properties, the blob theory implies that all such properties are universal functions of only a single concentration-dependent scaling variable. Based on this conjecture, Heo and Larson [J. Rheol. 49, 1117 (2005)] demonstrated earlier that normalized zero-shear viscosities of semi-dilute polymer solutions in good solvents lie on a universal scaling curve proposed by Rapsaud et al. [Macromolecules 28,927 (1995)]. Here we describe small-amplitude oscillatory shear measurements on polystyrene solutions in tricresyl phosphate at various C/C_e's, where C_e is the "entanglement concentration" which depends on molecular weight as C_e=\nu^{-1/3} with \nu the excluded volume exponent. Normalizing the complex shear moduli and frequencies (or shear rates) using the plateau modulus and the equilibration time, the linear and non-linear viscoelastic behavior of all semi-dilute solutions with the same C/C_e nearly collapse on the same plot, showing that the number of entanglements governs the rheology of all semi-dilute entangled polymer solutions in better-than-theta solvents.

Wednesday 11:25 Massachusetts
Ergodicity-breaking and glassy dynamics in the mixed flows of single polymer molecules
Eric S. Shaqfeh¹, Victor Beck², and Brendan Hoffman²
¹Departments of Chemical and Mechanical Engineering, Stanford University, Stanford, CA 94305, United States; ²Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United States
In this talk, the findings of Schroeder et al. 2003,, 2004 regarding the conformational hysteresis of single molecule dynamics near the coil-stretch transition in extensional flow will be reviewed from the point-of-view of Kramers' rate theory (or the Markovian first passage time) We will then apply these ideas to "mixed flows" which also theoretically create a coil-stretch transition. We will demonstrate that the coiled and stretched states are kinetically separated by an activation energy, and moreover that this general picture of polymer conformational changes...
dynamics as a first order activated process (e.g. by DeGennes, 1974) is changed in a significant way when there is vorticity in the flow. We will demonstrate that the addition of vorticity modifies these theories primarily by changing the size of the fluctuations in polymer length, thus providing a source of convective fluctuations. Thus vorticity in an otherwise extension dominant flow, can increase the "hopping" rate between conformational states in a manner that can be understood using advective (Taylor) dispersion theory. We will thus derive an effective Arrhenius expression for the rate of hopping from coiled to stretched and stretch to coiled polymer states analytically and describes the results of large scale compute simulations quantitatively including enhanced fluctuations in molecular length due to the Taylor dispersion in configuration. Furthermore we demonstrate that the activation energy in these Arrhenius expressions grows as $N_k$ where $N_k$ is the number of Kuhn steps in the chain and therefore ergodicity is broken in the limit $N_k \to \infty$. Thus the idea of glassy dynamic states must be included in any description of the rheology of this class of flows even for isolated chains.

**Symposium MF**

**Microfluidics, Confined Systems and Thin Films**

Organizers: Todd Squires and Nicos Martys

Wednesday 9:45 Connecticut

**Orientalional dynamics of polydiacetylene monolayers**

Alice Y. Wong¹, Jeyaprakash S. Samuel², An J. Goffin³, Sally Swanson³, J. Campbell Scott³, Bob Miller², and Gerald G. Fuller¹

¹Chemical Engineering, Stanford University, Stanford, CA, United States; ²Advanced Organic Materials, IBM Almaden Research Center, San Jose, CA, United States; ³Molecular Electronics, IBM Almaden Research Center, San Jose, CA, United States

Polyydiacetylenes (PDA) have gained popularity recently as unique materials with interesting electronic properties such as high non-linear optical susceptibility, ultrafast optical response, strong structural anisotropy and the chromogenic transitions arising from its fully p-conjugated system induced by a host of external stimuli such as heat, stress, pH and specific binding to biological targets. These features make them attractive for nanostructured devices in various applications such as chemical and biomolecular sensors. When properly oriented, diacetylene groups can undergo UV-induced photopolymerization to form an ene-yne alternating semiconducting polymer chain, resulting in highly ordered structures. The orientation of the polymer chains are critical to the properties of the film. In this study, monolayers of different PDA derivatives were photopolymerized and placed under extensional flow using rheological techniques such as the four-roll mill. Linear dichroism and Brewster angle microscopy (BAM) were used to explore the orientational dynamics of the different cross-linked polymers as the flow conditions were changed. The temperature and the surface pressure of the film at which polymerization occurs were also varied to observe the effects on film quality and domain formation. The monolayer was then deposited on a solid substrate using the conventional Langmuir-Blodgett transfer technique and the film morphology studied.

Wednesday 10:10 Connecticut

**Effects of temperature and chemical modification on polymer Langmuir films**

Grant T. Gavranovic, Meghaan M. Smith, Alice Y. Wong, and Gerald G. Fuller

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

Due to the balance of hydrophilic and hydrophobic interactions in each monomer unit, poly(tert-butyl methacrylate) (PtBMA) adopts 2-D conformations in the plane of the air-water interface. Langmuir films of PtBMA can be compressed to force a monolayer-to-multilayer transition that corresponds to a plateau in the surface pressure-area isotherm. We previously studied the rheology of Langmuir films of PtBMA at room temperature, and this work describes further studies on this system. Here, surface pressure-area (Π-A) isotherms and interfacial shear rheology experiments were performed to better understand the effects of two modifications: varying temperature between 5-40°C and partially hydrolyzing the polymer. Increased temperature produced isotherms with lower plateau surface pressures, $\Pi_p$, and $\Pi$-values shifted to lower areas above $\Pi_p$. Film properties transition from being primarily viscous to being dominated by elasticity as $\Pi_p$ is crossed for all temperatures studied, even as the value of $\Pi_p$ changes. Increasing the hydrolysis fraction leads to isotherms shifted to lower areas throughout the curve and higher $\Pi_p$ values. Both temperature variation and chemical modification are believed to affect the relative importance of polymer-polymer and polymer-subphase interactions.

Wednesday 10:35 Connecticut

**Thermoviscoelastic response of ultrathin polymer films: A nanobubble inflation method of determining the absolute creep compliance**

Gregory B. McKenna and Paul A. O'Connell

Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

There is a significant body of work suggesting that ultrathin polymer films (<100 nm in thickness) exhibit different properties from the bulk. In particular much work has shown that the glass transition temperature $T_g$ of nanometer thick polymer films can be dramatically reduced. Yet, there is little work that provides full thermoviscoelastic characterization of such materials. Here we describe a method, based on a miniaturization of the classic bubble inflation experiment, in which the absolute creep compliance of polymer films as thin as 13 nm has been measured. The presentation focuses on the apparatus itself, which uses the atomic force microscope to image the growth of micron sized...
bubbles. We also show results of viscoelastic characterization of poly(vinyl acetate)(PVAc) and polystyrene films (PS). Specifically, the PVAc films show little change in the segmental relaxation regime relative to the bulk, i.e., there is not a significant change in the Tg. On the other hand, for the PS the temperature regime at which glassy creep is observed is far below that of the bulk material (up to 50 K) for the thinnest films. Perhaps more interesting, the rubbery plateau compliance for both systems is found to be dramatically reduced for the thinnest films. Furthermore, the value of the plateau compliance is found to scale as approximately the square of the film thickness. The implications of the work will be discussed.

Wednesday 11:00 Connecticut

Evaporation induced self assembly and rheology change during sol-gel coating

Chang Lee and Amy Shen

Mechanical and Aerospace Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States

Thin films with self-assembled nanostructures are important in applications such as catalysis and biosensor technology. A major technique used to prepare such films is sol-gel processing. This technique involves depositing a complex fluid on a substrate by dip, spin, or spray coating, followed by allowing the film to evaporate and form self-assembled nanostructures. Since the composition of the film during coating is central to understanding how changing chemical and physical conditions affect the properties and microstructures of the films, we investigate the rheological properties of the entrained fluid film and its subsequent impact on the steady state film thickness during the evaporation-induced self-assembly process. We perform systematic experiments to measure the meniscus shape and film thickness during sol-gel dip coating. We observe that the experimental data of film thickness lies way below the LLD prediction from the classic film-coating results. To explain this discrepancy, we present a thin film model based on the lubrication approximation with evaporation effect. Our results show that evaporation-induced self-assembly leads to rheological variations in the entrained film and, consequently, alters the film thickness. The predicted film thickness based on the evaporation-induced rheology variation model compares well with the experiments.

Wednesday 11:25 Connecticut

Conformational anisotropy and glassy dynamics in polymer thin films

Folusho T. Oyerokun¹, Kenneth Schweizer², Anna Cavallo³, and Marcus Mueller⁴

¹Department of Chemical Engineering, University of California-Santa Barbara, Santa Barbara, CA, United States; ²Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, United States; ³Institute Charles Sadron, Strasbourg, France; ⁴Physics Department, Universitat Gottingen, Gottingen, Germany

A segmental level statistical mechanical theory has been developed for the ideal kinetic glass transition, or dynamic crossover, temperature in confined polymer films [1]. The theory is based on an anisotropic generalization of a coarse grained polymer mode coupling theory. Equilibrium conformational and thermodynamic information from the anisotropic Polymer Reference Interaction Site Model theory [2] and computer simulations quantifies the caging constraints. Confinement in a thin film geometry results in significant chain back-folding which commences at surprisingly large film thicknesses. This anisotropic conformational distortion is predicted to enhance the amplitude of thermal density fluctuations and the compressibility. For non-capped films (free standing or supported films on neutral substrates) the theory predicts a monotonous suppression of the crossover temperature with increasing confinement. The physical mechanism is a reduction of the degree of coil interpenetration and intermolecular repulsive contacts due to segmental alignment and deformation. The magnitude and film thickness dependence of the crossover temperature suppression is nonuniversal and controlled primarily by how confinement modifies local conformational statistics. An inverse apparent power law dependence of the ideal kinetic glass temperature shift on film thickness is predicted in reasonable agreement with a number of experiments. The theory can also be applied to dense grafted chain layers. In this case chain stretching is predicted to result in a reduction of compressibility or bulk modulus hardening, resulting in an increase of the ideal kinetic glass transition temperature relative to the analogous isotropic melt.


Symposium VS

Viscoelasticity of Solids, Thixotropy and Glasses

Organizers: Jan Mewis and Gregory McKenna

Wednesday 9:45 Rhode Island

The effect of applied strain during weathering exposure on the rheological properties of elastomers

Chris C. White, Kar T. Tan, David Benatti, and Donald Hunston

Building and Fire Research Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

A first step in developing a protocol to predict the in-service performance of elastomers involves understanding how the critical elements of outdoor weathering affect the degradation chemistry and mechanical properties. Elastomers experience chemical changes during outdoor exposure. The primary elements of the weather (temperature, humidity, Ultra Violet radiation, and mechanical stress) have been shown to affect the rate at which elastomers undergo chemical change. In this study we have exposed two different thermoplastic elastomers (SEBS and SBS) to
both controlled laboratory exposure and monitored outdoor exposure. The photooxidation chemistry was monitored using Fourier transform infrared spectroscopy. Modulus measurements on these samples were also performed and correlated to the photooxidation chemistry. The combination of SBS, ozone and mechanical strain produced significant cracking in the samples not seen in the SEBS strained or unstrained or SBS unstrained materials.

Wednesday 10:10 Rhode Island

A high strain rate tensile test instrument for rubber: Development and performance
Peter H. Mott, Howard Schrader, Jai A. Pathak, Daniel F. Roland, and C. M. Roland
Chemistry Division, U. S. Naval Research Laboratory, Washington, DC 20375-5342, United States

Various methods are applied to obtain the stress/strain response of elastomers at high strain rates. Extrapolation of low strain rate data is fraught with several limitations and is thus unreliable. Currently available experimental techniques include the split Hopkinson bar (SHB) and drop weight test methods. Here we describe the design and construction of a high strain rate tensile test instrument, which uses a falling weight to generate large deformation rates and increases the slider velocity by using a 4:1 lever for pulling the cables. Forces are measured by load cells and strain is optically determined by a high speed camera. Strain rates on the order of several hundred s\(^{-1}\) are achieved by the instrument, which fills in the hitherto unexplored strain rate window between quasi-static measurements on an Instron and the SHB (several thousand s\(^{-1}\)). We also describe the correction for inertia (arising from the finite mass of empty sample grips) and show data from this instrument for some model elastomers.

Wednesday 10:35 Rhode Island

Microstructure, rheological behavior and yield stress measurement of concentrated surfactants
Mickael Y. Castro\(^1\), Christopher W. Macosko\(^1\), David W. Giles\(^1\), and Teanoosh Moaddel\(^2\)
\(^1\)Department of Chemical Engineering and Materials Science, Univ. of Minnesota, Minneapolis, MN 55455, United States; \(^2\)Research and Development, Unilever, Trumbull, CT 06611, United States

Surfactants are of great importance in both the chemical industry and consumer sectors. They appear in areas including food, detergent, lubricants, emulsifiers, surface treatments, pharmaceutical products, emulsions, and many other commercial fields. One of the many roles of surfactants is rheology control, especially when present in concentrated form. An example is their role in controlling the extrusion process which is used to make soap bars. A model system was studied consisting of three pure surfactants: sodium stearate, sodium laurate, sodium oleate and water. The rheological properties and microstructures of the lyotropic crystalline phases were studied by dynamic shear experiments and by small angle x-ray scattering (SAXS). The effect of temperature and composition on the microstructure and rheological properties were investigated and related to bar processing performance. In particular the yield stress value of this system was studied and measured using several different methods. Capillary extrusion through orifice dies is a rapid method that relates well to the process. A new test was developed to measure the yield stress on a rotational rheometer utilizing a novelgeometry involving shear-fracture (cleavage) of extruded strands of the stiff paste material.

Wednesday 11:00 Rhode Island

Instrument compliance problems in linear viscoelasticity measurements
Chen-Yang Liu\(^1\), Roland Keunings\(^2\), Christian Bailly\(^1\), Ming Long Yao\(^3\), and Aly J. Franck\(^4\)
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Torsional compliance of the torque transducer can be an important issue in linear viscoelastic (LVE) measurements when the sample stiffness is high relative to the instrument stiffness. Gottlieb and Macosko [1] discussed the effect of instrument compliance on dynamic rheological measurements and possible corrections for mechanical transducers. For force rebalance torque (FRT) transducers, Mackay and Halley [2] also found that the angular compliance of the FRT could severely affect the dynamic moduli, because no feedback control servo system is instantaneous, and a combination of high frequency and torque (actually high stiffness) can lead to FRT compliance.

We evaluate compliance effects of the ARES 2K-FRT on LVE measurements by systematically comparing the results of the Frequency Sweep mode as well as strain and torque oscillation waveforms obtained with 25mm and 8mm plates respectively. It is a surprise that the 2K FRT even has a larger compliance than the corresponding mechanical transducer. Strictly speaking and without correction, the upper limit for the complex modulus \(G^*\) is close to 3 X 10\(^{5}\) Pa at 5\% uncertainty, when using 25 mm plates. This limit is smaller than the plateau modulus \((G_0^*)\) of most polymers. Therefore, to omit instrument compliance can lead to significant errors for \(G_0^*\) and wrong scalings for \(G^*\) in the plateau and Rouse regions. The respective roles of transducer and tool compliances are discussed. Tool compliance is a common problem for all rheometers using steel plates. Proper corrections have been incorporated in the new versions of the ARES firmware and data analysis program.

Shear waves generated by the motion of a sphere in a viscoelastic fluid
Hervé Tabuteau, Darek Sikorski, and John de Bruyn
Physics and Astronomy, University of Western Ontario, London, Canada

We have studied the dynamics of spheres impacting viscoelastic fluids as a function of sphere density and diameter as well as fluid properties. We present experimental observations of elastic shear waves generated by the supersonic motion of the sphere through the viscoelastic fluid. We show that these waves can last long enough to form standing waves in the sample container, and that the observed rebound and subsequent oscillations of the sphere can be explained in terms of these elastic waves.
Wednesday Afternoon

Symposium BE
Blends, Emulsions and Multiphase Flows
Organizers: Shelley Anna and Andy Kraynik

Wednesday 1:30 Vermont  BE6
Generating monodisperse droplets in water/oil/surfactant systems using micro- to macro-scale co-flow cells
Manuela R. Duxenneuner1, Justin J. Cooper-White2, Peter Fischer1, and Erich J. Windhab1
1Laboratory of Food Process Engineering, ETH Zurich, Institute of Food Science and Nutrition, Brisbane, QLD 4072, Australia; 2Division of Chemical Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

Monodisperse emulsions are highly sought-after in food process engineering and in industries required to produce well-structured multiphase systems. Small droplet sizes and a narrow size distribution are desirable characteristics of these emulsions. In the present work, a drop polydispersity of less than 1% was achieved using a co-flow geometry in which the dispersed phase was injected via a capillary into the continuous phase. Characteristics of the drop formation and breakup process were manipulated by changing parameters associated with the geometry (material and size of the capillary and continuous phase cell), flowrate (of both the dispersed phase and bulk phase) and properties of the fluids (viscosity, density, interfacial tension). A homologous series of TWEEN and sodium dodecyl sulphate (SDS) surfactant solutions (0.1 < ccmc < 500) and water were used to explore the role of the surfactants in the drop break-up event. It was found that at high velocity ratios (dispersed phase to continuous phase velocity), the drag forces imposed by the bulk fluid on the forming droplet dominated interfacial forces, suggesting that the presence of surfactant has little influence under these flow conditions. In this case, the drop size was highly monodisperse and was found to be only a weak function of flow rate. However at low velocity ratios, interfacial forces were found to dominate, resulting in the formation of satellite droplets. All drop break-up experiments were characterized in terms of the Weber (We), Reynolds (Re) and Capillary (Ca) numbers and the observed drop break-up behaviour was classified as either "dripping" or "jetting" regimes. The results of all experiments were used to determine the transition between these two regimes, which was best represented in terms of its position in We-Re-Ca space. The wide range of We, Re and Ca represented in the resulting phase space diagram makes it suitable for predicting the flow behaviour in a wide range of geometrically similar drop break-up devices.

Wednesday 1:55 Vermont  BE7
Dynamics of colloidal consolidation process inside an emulsion droplet
Danhong Wang1, Patrick Spicer2, and Amy Shen1
1Mechanical and Aerospace Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States; 2Complex Fluids Research, The Procter and Gamble Company, West Chester, OH 45609, United States

Dense packing of small clusters of microspheres proposed by Manoharan, et al. involves removal of fluid from the droplets (dispersed phase) into the continuous phase, which is referred to as the consolidation process. The consolidation process can be characterized as a diffusion process with moving boundaries. Therefore its dynamics is largely controlled by the diffusivity between the dispersed and continuous phases. In addition to the diffusivity, surfactant concentration and the number of particles inside the droplets might also change the dynamics of the consolidation process. In this work, we study the effects of surfactant concentration and particle number on the consolidation process. We found that if normalized by the initial droplet size and the consolidation time, the consolidation process obeys the same power law with the power coefficient of 1/2, regardless of the significant change in droplet diameter, as well as surfactant concentration and particle numbers. We also examine the consolidation behavior of anisotropic particles and compare with that of spheres.

Wednesday 2:20 Vermont  BE8
Influence of interfacial tension on the morphology of polymer blends
Carmela Tufano1, Gerrit W. Peters1, Peter Van Puyvelde2, and Han E. Meijer1
1Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands; 2Chemical Engineering, Katholieke Universiteit Leuven, Leuven, Belgium

The influence of a changing interfacial tension, based on diffusion of the polymeric chains of the components, on the morphology of polymer blends (PB/PDMS, PBD/PDMS) is experimentally investigated. The results are compared with the drop size evolution calculated from a drainage model, using either an immobile, partially mobile or fully mobile interface. Measurements of interfacial tension as function of time are carried out using a temperature controlled pendant/sessile drop apparatus. The time dependent drop shape is fitted using the Gauss-Laplace equation where interfacial tension is the fitting parameter. The blend morphology is studied with a well-defined flow history. Small Angle Light Scattering (SALS) measurements are used to obtain the time evolution of the droplet average radius by applying the Debye-Bueche theory and optical microscopy is performed to crosscheck the results. It is shown that the polymer pairs used in this work cannot be considered fully
immiscible and diffusion is always present. Interfacial tension changes significantly in time when the molecular weight of the dispersed phase is lower than the molecular weight of the continuous phase due to the migration of short molecules from the drop into the matrix. The results show that the larger the molecular weight asymmetry across the interface, the more the interfacial tension is eligible to changes. Reversing the phases, although a similar molecular weight asymmetry across the interface is present, interfacial tension shows a fast reduction and then evolves towards a steady-state value. This phenomenon can be correlated to a fast saturation of the inclusions. It is observed that depending on the type of interfacial response, the morphology development in the early stages is dominated by either diffusion or coalescence. Moreover, it is shown that existing sharp-interface drainage models do not apply for these types of blends.

Wednesday 2:45 Vermont

**Effects of compatibilizer on immiscible polymer blends near phase inversion**

Jeffrey D. Martin and Sachin S. Velankar

Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States

Block copolymers, termed compatibilizers, are often added to immiscible homopolymer blends to improve blending. The aim of this research is to quantify the effect of compatibilizer on the rheological properties of immiscible polymer blends having a droplet-matrix morphology with the droplet volume fractions approaching 50%. We used a stress-controlled rheometer to study steady shear viscosity, creep recovery after cessation of shear, and dynamic oscillatory behavior in poly(isobutylene) (PIB) / poly(dimethylsiloxane) (PDMS) blends with volume fractions ranging from 30% to 70% of PIB. Small amounts (0.01% to 0.5% by weight) of a PIB-PDMS diblock copolymer were added as compatibilizer.

Previous results on blends with less than 30% dispersed phase volume fraction show that the blend viscosity and recovery increase slightly with small amounts (less than 1%) of added compatibilizer. Both of these results are seen in higher dispersed phase volume fraction blends; however, the magnitude of these effects is far larger when the drop volume approaches 50%. For example, the relative viscosity of the compatibilized blends can be nearly a factor of two higher and the recovery can be as much as 50% higher than uncompatibilized blends, even with as little as 0.5% compatibilizer.

Furthermore, the block copolymer used was able to suppress droplet coalescence only if PIB was the continuous phase. This asymmetry in coalescence suppression led to an asymmetry in the rheological behavior. For example, the viscosities of the PIB in PDMS blends are slightly higher than those of the PDMS in PIB blends at the same dispersed phase volume fraction and compatibilizer loading, and the ultimate recoveries are much more sensitive to stress level for the PIB in PDMS blends.

In summary, we find that even small amounts of compatibilizer can have large rheological consequences which are of considerable relevance to polymer processing flows.

Wednesday 3:10 Vermont

**Coalescence suppression and interfacial tension in reactively compatibilized polymer blends**

Yanli Huo1, Gabriel Groeninckx2, and Paula Moldenaers1

1Department of Chemical Engineering, Katholieke Universiteit Leuven, Leuven B-3001, Belgium; 2Department of Chemistry, Katholieke Universiteit Leuven, Leuven B-3001, Belgium

Coalescence suppression was investigated in reactively compatibilized polypropylene (PP)/polystyrene (PS) blends. Polypropylene grafted with maleic anhydride (PP-g-MA) and amino-terminated polystyrene (PS-NH2) were used as reactive precursors to generate compatibilizers during mixing. A protocol of step-down in shear rate was applied to study the flow-induced coalescence. The shear flow was interrupted intermittently to probe the evolution of the morphology by rheological measurements (small amplitude oscillation test) and microscopy. The effect of compatibilizer on droplet coalescence was systematically studied, showing that the presence of compatibilizer suppresses the coalescence. The relaxation spectra were calculated from the dynamic moduli data, and an extra relaxation was observed in compatibilized blends, which shifted to lower time values with shear time during coalescence. Knowing the droplet size from in-situ microscopic observation independently, interfacial tension was calculated from the parameters obtained by fitting Palierne model to the dynamic moduli data. A reduction in interfacial tension was observed in compatibilized blends. Interfacial copolymer coverage was estimated to establish a relationship with the interfacial tension. The latter levels over the interfacial copolymer coverage range covered here.

Wednesday 4:00 Vermont

**Equilibrium dynamics of a polymer bicontinuous microemulsion**

Kristin L. Brinker1, Wesley R. Burghardt1, and Simon Mochrie2

1Northwestern University, Evanston, IL, United States; 2Yale University, New Haven, CT, United States

We report measurements of the equilibrium dynamics of fluctuating concentration in a polymer bicontinuous microemulsion. The microemulsion sample consists of a symmetric blend of polystyrene (PS) and polyisoprene (PI), compatibilized by a corresponding symmetric PS-PI diblock copolymer. Molecular weights and compositions are adjusted to access an equilibrium bicontinuous microemulsion phase. Although the individual homopolymer constituents are nearly Newtonian owing to their low molecular weight, the microemulsion exhibits pronounced viscoelasticity in small-amplitude oscillatory testing, owing to the interconnected morphology at length scales of 10s of nanometers. Exploiting the high coherence of the Advance Photon Source, x-ray photon correlation spectroscopy (XPCS) was used to study the dynamics of concentration fluctuations in this sample. At the temperatures studied, the autocorrelation function of the structure factor exhibits stretched-exponential relaxation behavior, with a relaxation time that depends strongly on scattering vector and temperature within the bicontinuous microemulsion phase. These results are compared to a time-dependent extension of the Teubner-Strey free energy expansion that is frequently...
used to describe the static structure factor of bicontinuous microemulsion samples. Further, we attempt to use this theory to connect structural dynamics measured by XPCS to the linear viscoelastic response of this sample.

Wednesday 4:25 Vermont

**Component terminal dynamics in PEO / PMMA blends**

Ilan Zeroni, Sahban Ozair, and Timothy P. Lodge

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

We present several methods of obtaining component terminal dynamics in miscible polymer blends using a commercial rheometer. These utilize steady and dynamic measurements of tracer blends, examining the relaxation of a few long chains in lower molecular weight blend matrices of varying composition. We apply these methods to PEO / PMMA blends. The results agree well with PEO diffusion data obtained from forced Rayleigh scattering. Results show that the mobility of PMMA is strongly affected by the presence of PEO, its monomeric friction factor dropping precipitously upon addition of small amounts of PEO. The mobility of PEO, on the other hand, is not as greatly affected by the presence of PMMA. The Lodge McLeish model, as usually applied, is unable to predict the observed behavior of either component. However, upon application of modified mixing rules, the data can be described almost quantitatively. We will discuss the implications of this approach.

Wednesday 4:50 Vermont

**Rheology and processing of LLDPE/LDPE blends: Long chain branching effects**

Delgadillo Omar1, Savvas G. Hatzikiriakos1, James J. Feng1, and Martin Sentmanat1

1Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC, Canada; 2Xpansion Instruments, Akron, OH, United States

The effect of long chain branching (LCB) on the miscibility, rheology and processing of LLDPE/LDPE blends was studied. The common LLDPE resin used in the blends was a hexene Ziegler-Natta having a Melt Index (MI) of 1 g/10min. This resin was blended with three different LDPEs having MIs of 7.5, 2.2 and 0.47, respectively. The prepared LLDPE/LDPE blends had weight compositions of 99/1, 95/5, 90/10, 80/20, 50/50 and 25/75. Master curves of linear viscoelastic moduli of all blends were constructed applying both vertical and horizontal shifts. The horizontal shift factors were obtained using an Arrhenius type equation and the activation flow energies, Ea, were calculated. It was found that Ea increases with the concentration of LCB in all three sets of blends. Furthermore, the blends containing high concentrations of LDPE, show enhancement of both, the elastic modulus, G', and complex viscosity, η*, at low frequencies, suggesting immiscibility. DSC on the blends confirms immiscibility by showing two distinct peaks which correspond to those of the pure resins; Moreover, in all cases, positive deviation from the log-additivity rule was observed. It was also found that shear rheology is unable to detect with certainty levels of LCB even in blends containing up to 20% of LDPE; on the other hand, extensional rheology was found to be very sensitive to levels of LCB even at blend compositions as low as 1% LDPE. Finally, the processability of all blends was studied in capillary extrusion in order to determine the effect of LCB on melt fracture phenomena. Various effects of LCB on the onset of melt fracture phenomena were found.

Wednesday 5:15 Vermont

**Crystallization of shape memory binary blends containing one crystallizable component**

Cheryl J. Campo and Patrick T. Mather

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PVDF:PMMA and PVDF:PVAc are semicrystalline-amorphous blends that demonstrate melt-miscibility. For shape memory applications, it is the PVDF crystallites that act as physical crosslinks by which a permanent or equilibrium shape can be set whereas the miscible amorphous component gives rise to temporary shape fixing. To gain control over the material response, it is important to understand how to tailor a system's given shape memory properties. For semicrystalline-amorphous blends, this can be achieved by detailed study of the effects of composition as well as the thermal histories to which such materials are subjected. We have studied the development of elasticity in such binary blends upon cooling below the equilibrium melting point of PVDF. In particular, we have observed gelation followed by development of a rubber plateau with significant dependence of kinetics on both degree of undercooling and composition. The modulus achieved is of paramount importance to shape memory behavior through the storage of elastic stress during the setting of a temporary shape prior to vitrification. The same samples have been characterized following completion of crystallization using creep testing in shear and tension. Within the context of quantitative shape memory characterization we will assess the correlation between viscoelasticity measured rheologically and the resultant shape recovery behavior.

Wednesday 5:40 Vermont

**Prediction of crystalline structure formation in flowing polymer melts**

Rudi J. Steenbakkers, Gerrit W. Peters, and Han E. Meijer

*Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands*

The effects of flow on the development of the semi-crystalline morphology, which to a large extent determines the fin properties of melt-processed polymers, are well documented but still not well understood. To bridge this gap and increase our understanding of the essential processes taking place on different length scales in a crystallizing melt, a multi-scale model for flow-induced crystallization (FIC) of polymers is being developed. Qualitatively, it appears possible to capture the influence of growing crystalline domains on the overall rheology by means of a soft-particle suspension model. However, for a quantitative validation we need to be able to calculate, based on the FIC model, 1) the number
density of spherulites, 2) the number density of oriented crystallites, 3) the length of oriented crystallites, and 4) the fraction of the material covered by crystallites (space filling) as a function of time. We developed a model for the flow-induced creation of meta-stable precursors and their transformation into stable crystalline nuclei, i.e. nucleation. This enables us to quantitatively predict the number density of spherulites and the resulting space filling, which is used as input in the suspension model. To obtain similar results for oriented crystallites, a multi-mode creation and growth model for the precursors, keeping track of the distribution of precursor lengths, is implemented. This is necessary because the length of a precursor at the moment of nucleation determines whether it will grow into a spherulite or an oriented crystallite. For different assumptions concerning the initiation and propagation of the longitudinal growth process, we demonstrate the predicted length distributions after different flow histories.

Symposium PS
Polymer Solution Rheology: Molecular-scale Modeling and Experiments
Organizers: Ron Larson and Jimmy Feng

Wednesday 1:30 Massachusetts PS5
Transient behavior of a tethered chain in uniform solvent flow
Aruna Mohan and Patrick S. Doyle
Department of Chemical Engineering, MIT, Cambridge, MA, United States

The response of a tethered polymer chain to uniform solvent flow is of interest in connection with the stretching and relaxation of single DNA molecules. This problem has been treated by Brochard-Wyart and coworkers (Brochard-Wyart, Europhys. Lett. 1993) with the use of scaling arguments. More recently, Zimmermann and coworkers (Rzehak et al., Eur. Phys. J. E 2000) have employed simulations to study the behavior of a tethered chain in uniform flow. However, the transient behavior of a tethered chain in uniform flow is not yet fully understood. Transient polymer unraveling is important in polymer-polymer collisions and DNA separations. In the present work, we perform Brownian dynamics simulations of a single, tethered bead-spring chain, with hydrodynamic interactions implemented via the Rotne-Prager tensor, and investigate the time-dependent response of the chain to uniform solvent flow.

Wednesday 1:55 Massachusetts PS6
Molecular simulation investigation of cross-stream migration of chain molecules in nanofluidic channels
Rajesh Khare
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States

The development of micro and nanofluidic devices for biomolecule manipulation has led to a significant interest in the transport phenomena at the molecular length scales. In particular, the phenomenon of flow induced cross-stream migration of polymer chains in nanochannels has suggested potential applications for DNA separation and sequencing operations. Our recent molecular dynamics simulation study (1) of shear flow of dilute polymer solutions in nanochannels has shown that such a cross-stream chain migration process is governed by three mechanisms: (a) chain-wall hydrodynamics (b) thermal diffusion and (c) gradients in chain mobility.

In our previous work, both polymer chain and the solvent were represented using a coarse grained model. The diffusion and hydrodynamic effects in the model system were determined by the intermolecular interactions; a purely repulsive Lennard-Jones potential was used for this purpose. In this work, we use molecular dynamics simulation to study shear flow of dilute polymer solutions in nanochannels by employing more realistic models for the polymer chain and the solvent molecules. Both static and dynamic properties of the system are used to assess the ability of these molecular models for representing the flow of a DNA solution in a nanochannel. Our results are used to determine the relative importance of a variety of factors such as the chain flexibility, chain length and solvent quality on the cross-stream migration phenomenon in nanofluidic devices.

The nonlinear rheology and shear banding of worm-like micellar solutions are studied and compared to results for polymer solutions. We present measurements of the micellar alignment and microstructure in solutions of cetyl pyridinium chloride in brine with added sodium salicylate that form viscoelastic solutions of wormlike micelles at rest. Previous work by Hu and Lips (JOR, 2005) demonstrated shear banding for this same solution. A special SANS flow cell enables the first direct measurements of the microstructure and micellar alignment in each individual band. These gap resolved 1-2 plane experiments demonstrate that the degree and orientation of segmental alignment of the micelles by the shear flow correlate with the measured shear viscosity. Combining the SANS measurements with flow-light scattering measurements shows that shear induces strong concentration fluctuations in the high shear band. The scattering in the fluctuating regime can be described by a surface fractal dimension similar to that observed in polymer solutions that exhibit shear induced concentration fluctuations. The results are contrasted with previous measurements on a surfactant solution that exhibits shear-induced phase separation. The shear-induced structures observed in the high shear band display quantitative similarities to measurements on semi-dilute polymer solutions under shear, suggesting scale invariance for shear-induced demixing. Differences are evident on shorter length scales, however, owing to the slower relaxation dynamics of the wormlike micelles compared to polymer solutions.
The dynamics of wormlike micelle solutions has been characterized rheo-optically. Two aqueous solutions were studied: one of cetyl pyridinium chloride (CPIc) and cetyl trimethyl ammonium bromide (CTAB), each with co-solute sodium salicylate. The principal dynamic timescales of these solutions were determined by linear rheometry, and the flow-induced birefringence was determined microscopically in planar elongational flow generated in a microfluidic cross-slot. The stress optic rule was observed at low rates. Moreover, the kinetics of alignment and relaxation were determined as fluid entered and exited from the extensional zone. As known previously, alignment requires accumulation of sufficient strain, so that peak birefringence is focused in a band along the line of stretching that intersects the stagnation point. As the flow rate increases, deviations from the stress optic rule occur. These become significant as the birefringence band changes shape and micellar alignment approaches saturation, at extensional Weissenberg number near unity. The stress optic rule must be applied with care, because these deviations are obscured somewhat when average birefringence is measured by sampling an area near the stagnation point. Finally, at slightly higher flow rate, symmetric planar elongation is unstable: micelles (and indeed the stretching axis) tilt away from the outflow axis, when the flow symmetry splits and inlet streams are directed predominantly to one or the other outlet channels.

Rheo-optics of equilibrium polymer solutions: Wormlike micelles in planar elongational flow generated in a microfluidic cross-slot
Jai A. Pathak1 and Steven D. Hudson2
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We revisit the classical problem of the viscoelastic response of nematic liquid crystal polymers to small amplitude oscillatory shear as described by the Doi-Hess mesoscopic orientation tensor model. First in the monodomain limit, using multiple timescale perturbation analysis, we describe a very slow timescale drift in the envelope of oscillations of the major director to one of two bistable asymptotic states, depending upon the initial value of the director angle. Additionally, this drift leads to a predicted long time decrease in the storage and loss moduli, consistent with the experimental observations in Moldenaers and Mewis, 1986, and Larson and Mead, 1989. Then we turn to nonhomogeneous liquids and examine the effect of spatial gradients in the director angle on the storage and loss moduli.
Wednesday Afternoon

**On solutions of Smoluchowski equation for solutions of rigid nematic polymers**

Qi Wang, M. Gregory Forest, and Ruhai Zhou

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The Smoluchowski equation is the transport equation for the probability density function for the rigid nematic polymers in a viscous solvent. We will discuss a solution method for solving the Smoluchowski equation with various intermolecular potentials, local and nonlocal alike in steady state. We will present the complete phase diagram for polar nematics for example, discuss the effect of imposed external fields and flow fields to spatially homogeneous and inhomogeneous nematic polymers solutions. Rheological predictions using the stress tensor derived through a virtual work principle will be discussed as well in various conditions.

**Symposium MF**

**Microfluidics, Confined Systems and Thin Films**

Organizers: Todd Squires and Nicos Martys

Wednesday 1:30 Connecticut

**Single drop dynamics in confined geometries**

Anja Vananroye, Peter Van Puyvelde, and Paula Moldenaers

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Recently, a trend towards miniaturization is emerging in the process industries. However, fundamental insight in micro-scale technologies, where the size of the dispersed phase becomes comparable to the dimensions of the channel, is lacking to a large extend. In this work, the effect of geometrical confinement on the dynamics of single droplets is investigated microscopically on a counterrotating parallel plate device in which it is possible to keep the droplet in a stagnation plane under flow. Microscopy images are recorded both in the velocity-velocity gradient and in the velocity-vorticity plane. Poly(dimethylsiloxane) droplets of varying sizes and viscosity ratio's are injected in a poly(isobutylene) matrix to study the deformation and orientation in simple shear flow as a function of capillary number. The dimensionless ratio of droplet diameter to gap spacing is used to quantify the degree of confinement and the results are compared with the predictions of the Maffettone-Minale model. It is observed that the deformation of confined droplets is still well predicted by the Maffette-Minale model for viscosity ratio's below one, but for viscosity ratio's above one, large deviations are present. Confined droplets are always more oriented in the flow direction than non-confined droplets. The start-up dynamics of confined droplets at near-critical capillary numbers shows overshoots in the drop deformation before reaching steady state. The results also indicate that droplet break up occurs at a higher capillary number with respect to the bulk critical capillary number for viscosity ratio's below one. This stabilization of the droplets is however not observed at high viscosity ratio's where droplet break-up is promoted by the confinement.

Wednesday 1:55 Connecticut

**Brownian dynamics simulations of the effect of polymer branching on electrophoresis through narrow constrictions**

Yong Min Lee and Yong L. Joo

Department of Chemical & Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

With the advancement of microfabrication technologies, the development of new microdevices aimed at the detection, sorting, and/or purification of individual molecules has become possible. One such device was recently designed by Han et al. for separation of DNA molecules by entropic trapping. The electrophoretic microchannel through which the DNA molecules are driven by an electric field consists of alternating wide (entropic) trapping regions and narrow constricted regions. Other experimental studies of DNA molecules undergoing electrophoresis in a matrix solution have shown that under certain conditions the electrophoretic mobility of three-arm star branched DNA can differ appreciably from that of a linear DNA molecule with comparable molecular weight. Yet often the relationship between polymer topology and properties is not well understood. To improve our understanding of the property-topology relationship of polymers in electrophoresis, we employ Brownian dynamics simulation of charged bead-spring chains to model the dynamics of charged polymers moving through an array of entropic traps, as employed by Han et al. in their experiments. In particular, we explore the effect of polymer branching topology on the time scales and mobility associated with the electrophoretic migration of the molecules through the microchannel. Moreover, we report findings on the influence of branching architecture on the modes by which the polymer molecules traverse the narrow channel.

Wednesday 2:20 Connecticut

**Single molecule visualization of polymers in flow through porous media**
Chad D. DeLong and David A. Hoagland

*Polymer Sci. & Eng., University of Massachusetts-Amherst, Amherst, MA, United States*

An open, nanofluidic system has been developed to drive flow through a packed bed of colloidal particles using capillary forces (wicking), allowing the study of polymer dynamics in the absence of the electric field that is typically used to drive micro- and nano-fluidic flows. Establishing flow without electric fields is important when dealing with charged molecules for which confirmation can be altered by the electric field or those insoluble in water (most synthetic polymers). In wicking flows, the flow rate decreases with the square root of time, so a wide range of flow rates are observed in the same system. Single molecule imaging was performed in this system on fluorescently labeled DNA using an optical microscope equipped with a fluorescent light source and CCD camera. The average polymer extension parallel to the flow increases with the Deborah number. At low Deborah numbers, fully relaxed conformations can be observed, while at high Deborah numbers, the polymers reach extensions comparable to their contour lengths. At sufficiently high flow rates, flow induced degradation can also be seen. The size of the particles used also played a critical role in the dynamics of the polymers in flow, with smaller particles leading to more hooking events causing more elongation of the polymer. Larger particles (diameter comparable to the contour length of polymer) caused much fewer hooking events leading to less elongation.

Wednesday 2:45 Connecticut

**Drop deformation in shear flow between parallel plates**
Pieter J. A. Janssen, Patrick D. Anderson, and Han E. Meijer

*MaTe, Eindhoven University of Technology, Eindhoven, Noord Brabant 5600 MB, The Netherlands*

Studying the nature of flow in confined geometries has become increasingly important due to downsizing of equipment. Examples include microfluidic devices as lab-on-a-chip, flow through porous media and heterogeneous flow of blood through fine arteries. Many of these applications involve fluids that consist of multiple phases (polymer blends, blood and biological mixtures), and hence the structure and structure development of these fluids is of great interest. Here, we focus on the flow of a single drop in a matrix fluid confined between two parallel walls, where the distance between the walls is in the order of the drop diameter. To model this system a 3-dimensional boundary integral method is used. The inclusion of two parallel walls in the boundary integral method is a non-trivial task. The free-space kernels normally used have to be modified to obey the no-slip condition at the walls, leading to quite complicated mathematical expressions. We limit ourselves to cases where the drop and the matrix have the same viscosity. The deformation of a drop in shear flow as function of the capillary number and the distance between the walls is studied. The drop shapes found in the presence of the walls substantially differ from the typical ellipsoidal shaped drops found in unbounded flows. Overall deformation, expressed in the Taylor deformation parameter, increases when reducing the distance between the walls. Furthermore, the angle of the major drop axis with the velocity direction also decreases. Despite larger deformation, the effect on the critical capillary number, however, is minimal. Finally, the effect of an insoluble surfactant is shown on deformation.

Wednesday 3:10 Connecticut

**Simulations of DNA electrophoretic stretching in microfluidic contractions**
Ju Min Kim and Patrick S. Doyle

*Department of Chemical Engineering, MIT, Cambridge, MA, United States*

Common motifs in micro/nano-fluidic electrophoresis devices are contractions and obstacles. Due to the insulating nature of the base materials, these shapes lead naturally to electric field gradients. We have developed a new numerical scheme to simulate DNA electrophoresis which couples FEM and Brownian dynamics. A target-induced searching algorithm is developed which allows for the use of unstructured finite element grids. We have used this method to study DNA stretching in hyperbolic contractions to compare to recent experiments of the same (Randall, Schultz and Doyle, Lab Chip 2006). Analysis of the field kinematics shows that certain DNA trajectories can accumulate a much greater strain than others and we use this information to design a more efficient DNA stretching device. The kinematics of the fields in the microfluidic devices are nonhomogeneous and we compare to stretching in fields with homogeneous kinematics. We will also discuss the stretching efficiency of the device as a function of Deborah number and DNA molecular weight.

Wednesday 4:00 Connecticut

**Effect of flexibility on the shear-induced migration of short polymers in parabolic channel flow**

David Saintillan1, Eric S. Shaqfeh2, and Eric Darve2

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There is now considerable evidence, both experimental (Chen et al. 2004, Fang et al. 2005) and via computer simulation (Jendrejack et al. 2003, 2004, Chen et al. 2004, Usta et al. 2005) that long-chain flexible polymers migrate toward the center line in plane Poiseuille flow owing to hydrodynamic interactions with the wall. The mechanism for this migration has recently been summarized by Ma and Graham 2005. Computational studies of rigid rod polymers (dePablo et al. 1992, Schiek and Shaqfeh 1997) have not included these hydrodynamic interactions and therefore have focused on migration toward the wall as a result of the configuration-dependent diffusivity that results from increased flow alignment in the near wall, high shear regions. To connect the studies of highly flexible polymers with those of rigid rod polymers, we study the effect of chain flexibility on the shear-induced migration of short polymers in a pressure-driven flow between two infinite flat plates. We have
implemented a Brownian dynamics algorithm that models a polymer molecule as a chain of N freely jointed Brownian rods and includes multibody hydrodynamic interactions between the chain segments and channel walls. Our simulations confirm the existence of shear-induced migration away from the solid boundaries toward the channel centerline as a result of wall hydrodynamic interactions, but we show the mechanism of this migration differs substantially if the chain is a rigid rod as opposed to a flexible thread. Thus the primary effect for very rigid polymers is still migration toward the walls. For flexible chains, we show that at a fixed ratio h/Rg of the channel width to the bulk radius of gyration, and at a fixed value of the Weissenberg number Wi, the migration is not significantly influenced by flexibility for the chain lengths considered in this work.

Wednesday Afternoon

Retention of polymer molecules in a cavity: A Lattice Boltzmann study

Hongbo Ma, Juan J. de Pablo, and Michael D. Graham

Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53705, United States

We study the retention problem in polymer solution flows in a porous media. As a simplified system, a bead-spring chain model of a dissolved polymer molecule confined between two solid walls with a cavity on one of them is considered. The solvent flow field is computed using the Lattice Boltzmann method, and each bead of the polymer chain is treated as a stokeslet. It is observed that the concentration inside the cavity is larger than that in the bulk flow. Previous theories argue that this concentration difference is because of the free energy difference due to the small stretch of the polymer molecule in the cavity. However, a recent kinetic theory identifies another migration mechanism based on the modification of the hydrodynamic interactions between the polymer molecule segments by the slit wall. Our simulation addresses this issue. The stretch of polymer molecule and normal stress of the flow inside and outside the cavity are obtained from the simulation. The hydrodynamic interactions are artificially turned on and off to reveal their importance. The final conclusion clarifies the origin of the retention of polymer molecules in porous media.

Confined diffusion of ds-DNA in slit-like nano-channels

Anthony G. Balducci¹, Pan Mao², Jongyoon Han³, and Patrick S. Doyle¹

¹Department of Chemical Engineering, MIT, Cambridge, MA, United States; ²Department of Mechanical Engineering, MIT, Cambridge, MA, United States; ³Dept of Electrical Engineering & Computer Science, MIT, Cambridge, MA, United States

The ability to controllably position and manipulate molecules in confinement is important in biomolecular separations and direct visual mapping of DNA. In order to optimally design such devices, the dynamics of molecules and their interactions with the solvent in confined geometries must be quantified. We present an experimental study of double-stranded DNA diffusion in slit-like channels under conditions of moderate (height ~ bulk radius of gyration of the DNA) to strong (height ~ persistence length) confinement. Scalings of diffusivity with channel height differ from blob model predictions. Scalings with molecular weight are indicative of hydrodynamic screening when the channel height is smaller than the bulk radius of gyration. We will discuss a scaling-level theory describing the origin of the observed free-draining diffusion dynamics. We find, after using a Zimm pre-average approximation, that hydrodynamic screening can result from a cancellation due to the unique symmetry of the disturbance flow-field in a slit as well as from the algebraic decay of the magnitude of the hydrodynamic interactions.

Structure and dynamics of multiphase flows in microchannels

Sara M. Hashmi¹, Michael Lowenberg², and Eric Dufresne³

¹Yale University, New Haven, CT, United States; ²Chemical Engineering, Yale University, New Haven, CT, United States; ³Mechanical Engineering, Yale University, New Haven, CT, United States

We investigate the impact of particles on the structure and dynamics of flows in microchannels. We are interested in non-Newtonian effects arising from fluid-particle and particle-particle interactions. These interactions can have a large impact on the macroscale transport of complex fluids through microchannels, and are known to play an important role in the normal physiology of blood flow. We have developed a novel confocal microscope that enables the imaging of flowing suspensions with 10 kHz temporal resolution. Subsequent analysis yields velocity and volume fraction profiles in cross-section. Here, we present preliminary results on the behavior of hard sphere systems over a range of volume fractions.

Particle migration in 1D, 2D, and 3D microchannel flows

James F. Gilchrist and Changbao Gao

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

Shear-driven particle migration is investigated in steady pressure-driven flows. In 100x40 micron channels, self-organization of 1 micron charge-stabilized colloidal microspheres occurs due to particle migration, a well-understood phenomena in simple flows, typically driving particles away from the walls toward the center of the channel despite Brownian and collisional diffusion. Flow in the transverse direction is generated by recessed herringbones in the top of the channel (Stroock et al, Science, 2001), significantly enhancing mixing. This combination of mixing and self-organization results in nontrivial concentration patterns. Using high-speed confocal laser scanning microscopy, we directly image the microspheres to measure the averaged 3D spatial concentration profile. In addition, we are able to locate individual particles and...
determine the local particle positions to reaffirm local concentrations and investigate particle interactions, local 3D velocity, and suspension structure as a function of the underlying flow topology, bulk concentration, and Reynolds and Péclet number.

**Symposium GP**
**General Papers**

Organizers: Jason Butler and Phil Sullivan

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**Wednesday 1:30** Rhode Island

**Rigid random coils of carbon nanotubes**

Heon Sang Lee¹, Chang Hun Yun¹, Heon Mo Kim¹, Min Park², and Hyunjung Lee²

¹Research Park, Engineering Plastics R&D, LG Chem, Daejeon 305-380, Republic of Korea; ²Korea Institute of Science and Technology, Seoul, Republic of Korea

A perfect carbon nanotube (CNT) is a straightforward tubular mesoscopic shape. When the contour length of the CNT is much longer than its bending persistence length, the CNT can be considered as a semi-flexible chain having Kuhn lengths equal to twice the bending persistence length. A carbon nanotube can be permanently bent by exerting an electric field. It is also possible that a CNT has permanent bending points along the CNT axis. A rigid random coil has the permanent bending points which are randomly distributed along the axis. In this work we show that the intrinsic viscosity of the rigid random coils scaled with the overall size of the particles. And the overall size of the particles depends on the bending ratio (the degree of bending points and their distribution) as well as the contour length. We will also address the model to predict the intrinsic viscosity of the rigid random coils.

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**Wednesday 1:55** Rhode Island

**Understanding polymer nanofiber electrospinning: Kinematic measurements and dimensional analysis**

Matthew E. Helgeson, Kristie N. Grammatikos, Norman J. Wagner, and Joseph M. Deitzel

University of Delaware, Newark, DE 19716, United States

Polymer electrospinning has gained much attention for its ability to produce polymer and composite nanofibers from a solution or melt. However, electrospinning behavior arising from complex interactions between electrostatics, non-Newtonian rheology, and free surface flows is poorly understood. The present work outlines the results of recent efforts aimed at developing and experimentally verifying an engineering understanding of the electrospinning process. High speed videography was used for the direct measurement of the kinematics of electrospinning jets of aqueous poly(ethylene oxide) seeded with tracer particles under various operating conditions. The results of particle tracking velocimetry validate several important assumptions and conclusions typically found in analytical models for electrospinning. Specifically, the assumptions of negligible mass transfer and the slender body approximation are experimentally verified. Further, we find that the jet profile asymptotes to the scaling predicted by electrohydrodynamic theory. Additionally, the velocity profile in the developing jet follows that expected for steady uniaxial extensional flow near the jet origin, thus defining an effective rate of extension for electrospinning. The extension rate is correlated with process conditions and solution rheology, and trends in the jet morphology are argued in terms of strain hardening of the electrospinning fluid. Finally, using previously developed electrohydrodynamic models as a framework, a semi-empirical dimensional analysis of the electrospinning process is developed and applied to electrospinning data taken for several polymer-solvent systems presented in the literature. The results show universal behavior that correlates process parameters and fluid properties to ultimate fiber morphology.

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**Wednesday 2:20** Rhode Island

**Modeling polymer melts containing short and long glass fibers: Part I Transient rheology**

Aaron P. Eberle¹, Gregorio M. Velez², Donald G. Baird¹, and Peter Wapperom³

¹Chemical Engineering, Virginia Tech, Blacksburg, VA 24061, United States; ²Macromolecular Science and Engineering Department, Virginia Tech, Blacksburg, VA 24061, United States; ³Mathematics Department, Virginia Tech, Blacksburg, VA 24061-0123, United States

In this paper we investigate the transient shear rheology of polypropylene (PP) and polybutylene terephthalate (PBT) containing short glass fibers (30% wt., initial lengths of 1mm, 2mm, and L/D of 80, 16 respectively) and PP containing long glass fibers (40% wt., initial length of 11mm and L/D of 647). The objectives of this work are to determine the relation between stress growth and relaxation behavior to fiber orientation, interaction and matrix rheology and model the behavior by extending the Doi theory for rigid rod molecules in a Newtonian solvent to glass fibers in a non-Newtonian matrix. Doi's original theory predicts some of the interesting transient phenomena exhibited by the composite materials, but the theory predicts that the relaxation processes are governed by the reorganization of the fibers due to the Brownian motion contribution. Brownian motion can only be a factor if the characteristic dimension is sufficiently small, less than 500nm. In order to correctly predict the transient rheology of these materials, the Phan Thien-Tanner (PTT) model is used to model the rheology of the composite, where the contributions of the fibers is absorbed into the enhanced relaxation spectra. The fiber orientation is then calculated by incorporating the predicted flow field into Doi theory neglecting the effects of Brownian motion. Material parameters for the theory are found by fitting the model to dynamic and steady shear measurements performed on an RMS-800 equipped with cone and plate geometry for small fiber samples, and parallel plate geometry for long fiber samples to allow for gap control. Intermittent stress growth experiments are used to elucidate the
contribution of the viscoelastic matrix and glass fiber to the relaxation process. It is confirmed that Brownian motion does not play a role in the relaxation processes but is most likely due to the relaxation of the polymer chains.

Wednesday  2:45  Rhode Island  GP4

In situ synchrotron studies of structure development during injection molding of a liquid crystalline polymer

Wesley R. Burghardt and Stanley Rendon
Northwestern University, Evanston, IL, United States

As in all polymer materials, the effect of polymer processing on the underlying molecular structure has a profound effect on the properties of liquid crystalline polymer products. While in situ scattering techniques have proven powerful for studying complex polymer structure during comparatively simple shearing or channel flows, their application to processing flows has largely been limited to in situ x-ray scattering/diffraction studies of structure development during fiber spinning. Here we report a new experiment in which a lab-scale injection molding machine has been modified to allow real-time, in situ measurements of molecular orientation development and subsequent crystallization during injection molding. The experiment requires high x-ray energy to reduce absorption in the aluminum mold wall, and high flux and a fast area detectors to achieve the necessary resolution to track time-dependent changes in fluid structure during mold filling. Hence it is ideally suited to the capabilities of the Advanced Photon Source. We report measurements injection molding of a commercial liquid crystalline copolyester (Vectra A) as a function of position in the mold and various process variables.

Wednesday  3:10  Rhode Island  GP5

Some considerations on aspects of yield stress based on computational modeling

Nicos S. Martys
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In this presentation some issues concerning the interpretation of yield stress measurements are considered using the computer simulation of model hard sphere suspensions with Van der Waals interactions. Fits to phenomenological equations (Brinkman, Hershel Buckley and Casson equations) are compared. Other measures of yield stress, based on stress growth curves, are examined. Depending on the degree of strain, physics at different length scales are probed ranging from scales associated with interparticle interactions up to strains associated with breaking up of clusters due to excluded volume or jamming like effects.

Wednesday  4:00  Rhode Island  GP6

Shear and effective elongational rheology and polymer molecular characteristics

Xiaoling Wei¹, John R. Collier², and Simioan Petrovan²
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Extensional deformations play a significant role in many processing operations which involve a rapid change of shape such as fiber spinning, film blowing, blow molding, and nonwoven melt processing. To develop real time, on-line process and quality control analysis in these operations, knowledge of the effects of molecular characteristics and processing conditions on the elongational rheology is essential. In this work, shear rheology of six polyethylenes (PE) and one polysisobutylene (PIB) was measured at different temperatures using a rotational rheometer. Effective elongational viscosity of polyethylenes and polysisobutylene was measured at different Hencky strains and temperatures using a capillary rheometer by replacing the capillary cylindrical die with a hyperbolic converging die. The hyperbolic shape of the die establishes a purely elongational flow field at a constant elongational strain rate throughout the die. The effects of molecular characteristics such as molecular weight, molecular weight distribution, and long chain branches and the processing conditions such as temperature and Hencky strain on the elongational rheology of PE and PIB samples were studied. The results from the hyperbolic dies were compared with results from other techniques, namely Rheometrics Extensional Rheometer (RER) and Elongational Rheometer for Melts (RME). Good master curves were created for the temperature shifting, Hencky strain shifting, and simultaneous temperature and Hencky strain shifting of effective elongational viscosity.

Wednesday  4:25  Rhode Island  GP7

Investigating the steady and transient non-linear rheology of wormlike micellar solutions

Christopher J. Pipe, Nahn Ju Kim, and Gareth H. McKinley
Hatsopoulos Microfluids Laboratory, Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Despite 30 years of study, the complete constitutive response of wormlike micellar solutions is far from understood. In small amplitude deformations the response of many micellar systems is well described by a single mode Maxwell model, in agreement with the fast breaking limit described by Cates. In steady shear flows, numerous measurements have shown these materials may shear-thicken and/or shear-band; however, there are few qualitative comparisons with constitutive models. In this study we probe the linear and non-linear rheological responses of cetylpyridinium chloride (100 mM) / sodium salicylate (50 mM) wormlike micellar solutions in both controlled stress and controlled strain rheometers. Experiments are also performed using a capillary breakup extensional rheometer (CABER) with the aim of creating a complete data
set covering a wide range of deformation histories for comparison with a new two species non-affine network model developed by Cook and coworkers.

Initially, we consider shear stress and first normal stress difference data from steady state shear experiments in a cone and plate apparatus, including measurements of the radial pressure distribution which are used to calculate the second normal stress difference. Next we examine the transient response to step shear strains of increasing amplitude, in addition to step shear rates and step shear stresses. Such measurements can be used to construct phase plane plots and three-dimensional surfaces that characterize the material evolution in stress-rate-time space. In light of this, we discuss results from large amplitude oscillatory stress perturbations about the zero stress point and also around the critical stress for shear banding. Finally, we compare the behavior of micellar solutions after a step shear strain and after a step extensional strain.

Wednesday 4:50 Rhode Island
Shear induced long-range alignment of BCC ordered block-copolymers
Prashant Mandare and H. H. Winter
Chemical Engineering, University of Massachusetts, Amherst, MA 01003, United States

The present study deals with effect of large shear on an asymmetric block copolymer that forms BCC structure in nanophase separated state. The material studied is poly(styrene)-poly(ethylene butylene)-poly(styrene) swollen in a solvent that is selective for the midblock. Dynamics of recovery after shearing are followed by rheology and the final morphology was determined by SAXS. Shearing at constant shear rate and by large amplitude oscillatory shear (LAOS) leads to destruction of the BCC lattice. The structure is able to recover upon cessation of shear. The recovery kinetics after cessation of shearing at constant rate as well as after LAOS with strain amplitude that is greater than 1.0 are very similar to the one following thermal quench from above nanophase separation temperature. LAOS with a strain amplitude less than or equal to 1.0 leads to formation of highly ordered structures. The sample can be aligned with LAOS at either low frequencies where BCC plateau is observed in $G'$ or at higher frequencies where $G'$ and $G''$ run parallel to each other. The orientation of the aligned sample depends on shearing frequency, strain and temperature. At low frequencies, a six-fold pattern is observed corresponding to $\{110\}/<111>$ domain texture whereas a four-fold pattern is observed at higher frequencies corresponding to $\{111\}/<112>$ domain texture.

Wednesday 5:15 Rhode Island
Mechanical hole burning spectroscopy in block copolymers: Hole burning through the order-disorder transition
Gregory B. McKenna$^1$, Qian Qin$^1$, and Xiangfu Shi$^2$
$^{1}$Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121, United States; $^2$Molecular Genetics & Cell Biology Dept, University of Chicago, Chicago, IL 60637, United States

We have developed a Mechanical Spectral Hole Burning (MSHB) technique to investigate the dynamic heterogeneity of polymeric materials. In this technique, a mechanical pump perturbation is applied to the sample to excite the dynamic heterogeneities and this is followed by a small linear strain. Comparison between linear response after perturbation and that without any perturbation can result in vertical and horizontal modifications in the response that are referred to as "holes". The holes are a signature of dynamic heterogeneity in complex fluids such as polymers. Unlike its dielectric analogue, MSHB can be used to characterize materials having a weak dielectric response and is, therefore, a potentially powerful technique to probe heterogeneity. Here we attempt to establish a quantitative relationship between the heterogeneity and its corresponding length scale, by developing a "calibration" for the dynamic heterogeneity, i.e. the frequency and magnitude of the burned hole and the size or length scale of the heterogeneity. We consider block copolymers in the vicinity of the order-disorder transition temperature. We interrogate these materials using the MSHB method at different temperatures going through the phase boundary. For a styrene-isoprene-styrene triblock copolymer where the isoprene block is well entangled, it was found that the amplitudes of burned holes increase as the phase boundary is approached from the one-phase region to the two-phase region, i.e., as the order-disorder transition is traversed. On the other hand, for a styrene-isoprene diblock copolymer with weakly entangled isoprene block, no apparent holes can be observed, even in the heterogeneous (two phase) regime. Therefore, the mechanical holes detected by MSHB seem to be sensitive to the entanglements of polymer systems, not the "blockiness". Further work is ongoing to use miscible blends and other block copolymer systems to determine if the MSHB response can be quantitatively related to the known heterogeneities of the systems.

Wednesday 5:40 Rhode Island
On-line characterisation of small-scale polymer processing
Joao M. Maia, Paulo Teixeira, Jose A. Covas, and Olga S. Carneiro
Department of Polymer Engineering, University of Minho, Guimaraes, Portugal

Extruders are a fundamental part of any extrusion and compounding line. Single-screw extruders are of general-purpose application, while intermeshing twin-screw machines have found special application niches, where their characteristics are used with greater advantage. Counter-rotating extruders are nowadays the standard choice for extruding PVC dry blends. The co-rotating solution is often used for compounding operations, mainly because of its good mixing capabilities, and the fact that characteristics like residence time or shear level can be controlled by exploring the geometrical flexibility of the equipment and the range of applicable processing conditions. These capabilities have led co-rotating extrusion to be the technique of choice in industrial applicability studies of novel systems, e.g., polymer/nanoclay and polymer/nanotube composites and reactive blends. However, due to either the small quantities of materials available or their high cost, it is often necessary to have the capability to perform this work at small, laboratory scales. The aim of this work is to meet the above goal with a novel small-scale modular
single / twin-screw extrusion system, with well-controlled outputs in the range 100-500 g/h and the capability to perform material characterization on-line. This mini-extruder is equipped with ports that allow sample collection or non-intrusive analysis, e.g., RTD, to be performed along its axis at desired locations. This system is coupled to a modular slit die that allows a wide range of rheometrical functions, e.g., shear viscosity and normal-stress differences, to be measured and rheo-optical experiments to be performed. Results are shown and the concept validated for a number of simple and complex systems, including different homopolymers and multi-phase systems (nanocomposites and reactive blends).
Thursday Morning

Symposium BE
Blends, Emulsions and Multiphase Flows
Organizers: Shelley Anna and Andy Kraynik

Thursday 8:05 Vermont BE16
Shear-thickening of an emulsion stabilized with hydrophilic silica particles
Bettina Wolf, William J. Frith, and Mark Kirkland
1Division of Food Sciences, University of Nottingham, Loughborough LE12 5RD, United Kingdom; 2Corporate Research, Unilever, Bedford MK44 1LQ, United Kingdom; 3Measurement Science, Unilever, Bedford MK44 1LQ, United Kingdom

The rheological behavior of classical emulsions stabilized with amphiphilic molecules, emulsifiers or surfactants, is typically shear-thinning. Depending on the phase volume of the internal droplet phase and the material properties of the continuous phase a low shear viscosity plateau or yield behavior, and, occasionally, a high shear viscosity plateau is observed. Classical shear-thickening behavior caused by formation of jammed networks as observed for suspensions with high particle phase volumes is not shown by emulsions. In this paper, a first insight in the rheological behavior of particle stabilized emulsions in steady shear flow is presented. The emulsions were designed for systematic rheological investigation and above all, they were formulated to be stable against coalescence in shear flow. For simplicity, hydrophilic silica particles commercially available as an aqueous dispersion were used. The diameter of these particles is in the order of 10 nm. The rheological characterization of the emulsion, restricted to steady shear, is complemented by structural analysis of the particle layer at the droplet (oil-water) interface using cryo SEM. To emphasize the unusualness of the flow behavior found here for an emulsion system, albeit a particle stabilized emulsion, data for an equivalent emulsifier stabilized emulsion are also presented.

Thursday 8:30 Vermont BE17
Stability and rheology of particle stabilised emulsions produced using hydrophilic silica particles in the presence of multivalent cations
William J. Frith, Roman Pichot, Mark Kirkland, and Bettina Wolf
1Unilever Corporate Research, Sharnbrook, Bedfordshire MK44 1LQ, United Kingdom; 2Measurement Science, Unilever, Bedford MK44 1LQ, United Kingdom; 3Division of Food Sciences, University of Nottingham, Loughborough LE12 5RD, United Kingdom

Much of the published literature on particle stabilized emulsions has centered on the use of partially hydrophicised silica particles as a model system. Whilst these materials offer many advantages in terms of flexibility, they are somewhat laborious to prepare. Here, we explore the ability of 'hydrophilic', (i.e. not surface modified) colloidal silica particles to stabilize O/W emulsions in the presence of a range of cations. Whilst it has been shown that lowering pH can render nano-sized silica (~10nm) sufficiently hydrophobic so as to stabilize O/W emulsions (Wolf et al., this meeting), this method does not appear to generalize to larger silica particles (~200nm). Following previous work by Wu et al. [1] and Binks et al. [2] it appears that certain cations will render various inorganic oxide surfaces more hydrophobic. In particular it appears that Lanthanum renders silica sufficiently hydrophobic to stabilize O/W emulsions. As such this makes the combination of Stober silica particles with appropriate concentrations of Lanthanum cations an attractive model system for the study of the rheological behavior of Pickering emulsions. We present initial investigations exploring the formulation space of such emulsions, and how their rheology and stability compare with more conventional emulsions. We find that for emulsions stabilized with 220nm Stober silica, the total emulsion interfacial area is determined by the concentration of the silica particles. Microscopic examination indicates that the particles have formed a close packed monolayer on the droplets, and no free particles are present, making this an 'ideal' Pickering emulsion. The particles appear to form a rigid shell around the droplets, making the rheological response of the emulsions more similar to that of a classical suspension than of a surfactant stabilized emulsion.

simulated. We present the results, with emphasis on the fluctuating values of the wall shear stress downstream of the stenosis. These values are compared to the wall shear stresses computed assuming Newtonian behavior.

While the flow rate-pressure drop relationship for single-phase microfluidic flow of a Newtonian liquid is quite straightforward (since Re is small), it can be complicated for the case of two-phase droplet type flows. We characterized the flow-pressure relationship for the single-file flow of water drops in oil in microfluidic channels of rectangular cross sections. The pressure for such droplet flows was always larger, sometimes over 50% larger than that for corresponding single-phase flows of the continuous phase. This is in spite of the fact that the water drops had a substantially lower viscosity than the continuous phase oil. The excess pressure was found to correlate reasonably well with the size of the drops relative to the size of the channels. This correlation for the excess pressure, as well as a correlation presented here for the size of drops in microchannels, should provide convenient guidelines in designing microfluidic devices for two-phase flows.

Much recent research on microfluidics has focused on two-phase flows. This often involves generating and then conveying a single file flow of drops in microfluidic channels. Here we ask the question: what is the effective viscosity of such a two phase flow? I.e. what is the relationship between flow rate and pressure drop? Such knowledge would be useful, e.g. in designing on-chip microfluidic pumps.

We investigate temporal heterogeneities in the dynamics of coarsening foams, applying the recently introduced Time Resolved Correlation scheme [1] to the intensity fluctuations of multiply scattered light. We find that the dynamics is determined by two distinct processes: a quasi-continuous one, which we attribute to small displacements of the bubble interfaces, and an intermittent one, which we attribute to local, avalanche-like bubble rearrangements. Although the rearranged regions are much smaller than the scattering volume, these rearrangements are observed to occur quasi-periodically; this suggests that a local rearrangement releases internal stresses over regions that exceed the scattering volume and thus are significantly larger than the size of the rearranged zone itself.

Thursday 11:00 Vermont

**Simulation of bubble growth in polymer foaming**

Pengtao Yue¹, James J. Feng¹, and Christopher A. Bertelo²

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Bubble growth plays an important role in determining the cell size distribution in thermoplastic foams. In this work, the diffusion-driven bubble growth in a polymer melt is computed by direct numerical simulation. The pressure and mass inside each bubble follow the equation of state for an ideal gas. A finite element method is used to calculate the gas concentration and flow variables in the polymer melt. Henry's law is employed to relate the bubble pressure and the gas concentration at the bubble surface. An Arbitrary Lagrangian-Eulerian (ALE) technique is used to handle the moving boundary. Within each time step, the whole system is solved iteratively. By modeling the polymer melts as Oldroyd-B fluids, we will study the influence of rheology on single bubble growth and interactions between multiple bubbles.

Thursday 11:25 Vermont

**The shear modulus of particle-laden foam**

Andrew M. Kraynik¹, Sylvie Cohen-Addad², Reinhard Rohler², and Douglas A. Reinelt³

¹Multiphase Transport Processes Department, Sandia National Laboratories, Albuquerque, NM 87185-0836, United States; ²Laboratoire Physique des Matériaux Divisés et des Interfaces, University of Marne-la-Vallee, Marne-la-Vallee, France; ³Department of Mathematics, Southern Methodist University, Dallas, TX, United States

Recent experiments indicate that Gillette shaving cream becomes stiffer with the addition of solid particles that are comparable in size to the foam bubbles, but the magnitude of the effect decreases as the relative particle size increases. We are using Surface Evolver simulations to investigate this scale-dependent behavior. The dry three-dimensional foam structure ranges from ordered to disordered. The solid particles are modeled as bubbles with higher surface tension than the foam; the ratio of particle to bubble volume: \( V_p/V_b = 1, 8 \). The high-tension drops approach spherical shape when the relative surface tension is large. We find that the shear modulus of foam increases as the concentration and surface tension of the particles increases. The magnitude of effect decreases as particle size increases, in agreement with the experiments, however, the simulations predict a much smaller enhancement in modulus. Slip at the particle surface appears to contribute to the discrepancy.

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

Thursday 11:50 Vermont

**The shape of bubbles and drops rising in a nematic liquid crystal**

Chunfeng Zhou¹, Pengtao Yue¹, James J. Feng¹, Chun Liu², and Jie Shen³

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This work is motivated by recent experimental observation of unusual "inverted-heart" shapes that a bubble assumes when rising in an anisotropic fluid. A possible explanation is in terms of the molecular orientation of the matrix fluid with respect to the bubble surface. In this work, we use numerical simulations to test such a hypothesis. The moving interface problem is formulated in a diffuse-interface framework. The anisotropic fluid is represented by a simplified Leslie-Ericksen theory for nematic liquid crystals, with director anchoring on the surface of an isotropic drop. The simulations are carried out using axisymmetric finite elements. Results show an array of drop shapes, depending on the interplay among inertial, capillary, anchoring and elastic effects. Drops with sufficiently strong planar anchoring and moderate elasticity rising in a medium with vertical far-field orientation assume the inverted-heart observed in experiments. This is shown to be mainly due to the competition between interfacial tension, anchoring energy and bulk elastic energy. Furthermore, two boojum defects appear on the upper and lower poles. The size of the defects plays a significant role in shaping the rising bubble.

Thursday 12:15 Vermont

**Dynamic interfacial tensiometry**

Steven D. Hudson¹ and Jai A. Pathak²

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Microfluidic interfacial tensiometry was developed recently, and applied to simple fluids and their mixtures. Here we exploit microfluidics’ inherent relationship between time and space to demonstrate its ability to measure time dependence of the interfacial tension of a dilute aqueous solution of butanol in oil (the latter being either canola or silicone oil). Butanol is surface active and reduces the interfacial tension. However, as time passes, butanol transfers to the oil phase, where it is more soluble, causing a decrease in its interfacial concentration, and a rising interfacial tension. The kinetics of this process on the time scale of approximately one second is here measured and modeled effectively.
Thursday 8:05 Massachusetts

**Probing the origin of nonlinear velocity profiles in shear flow of entangled polymers**

Sham Sundar Ravindranath and Shi-Qing Wang  
*Polymer Science, University of Akron, Akron, OH 44325, United States*

Following the initial experiments[1] to probe the velocity profile during shear of entangled polymer solutions we carry out more systematic experiments to determine any difference in the resulting flow fields in response to controlled-displacement shear and controlled stress shear respectively. In particular, we are interested in identifying the condition, under which application of a constant stress would result in a homogeneous shear field in entangled polymers. Even when imposed shear stress would result in initial shear banding in the velocity profile, we are interested to find whether it returns to linearity at long times (i.e., in steady state) under a constant stress.


Thursday 8:55 Massachusetts

**Opening the black box of large step strain experiments**

Shi-Qing Wang and Sham Sundar Ravindranath  
*Polymer Science, University of Akron, Akron, OH 44325, United States*

The observed agreement [1] between experiment and theory for large step strain tests on entangled polymer solutions has been widely regarded an indication of the success of the paradigm based on the tube model. However, our perception of how chain entanglements get rearranged in shear flow has led us to subject such a popular experiment to direct flow visualization. Using an effective particle-tracking-velocimetric method we show that entangled polymer solutions suffer structural breakdown upon a step shear, thus providing the most striking and convincing evidence of chain disentanglement due to strong externally imposed deformations [2]. This collapse of the entanglement network occurs at step strains as low as 100%, whereas previous experimental and theoretical studies have assumed perfect structural integrity of such materials for strains as high as 1000%. The disintegration of the entanglement network leads to inhomogeneous macroscopic flow of the sample after cessation of shear. The collapse of chain entanglement network is also observed during a large step strain. As a second example to provide an interesting, we have also studied the stress relaxation behavior of entangled polymer melts in a customer-made sliding plate rheometer. In absence of an interfacial failure, the onset strain for rapid stress relaxation due to network disintegration is considerably higher than observed for the entangled solutions.


Thursday 9:20 Massachusetts

**Generalized Brownian configuration fields for Fokker-Planck equations including center-of-mass diffusion**

Jay D. Schieber  
*Illinois Institute of Technology, Center of Excellence in Polymer Science and Engineering, Chicago, IL 60616, United States*

Hulsen, et al. [J. Non-Newtonian Fluid Mech. 70, 79-101 (1997)] introduced the concept of Brownian Configuration Fields for the simulation of stochastic models and flows in complex geometries. Even for homogeneous flows, stochastic models require numerical simulation of either the Fokker-Planck Equation, or their equivalent stochastic differential equations. Brownian configuration fields represented a major advance to combined micro/macro or CONNFFESSIT methods, allowing excellent variance reduction in calculation of non-homogeneous flows. We present an alternative argument to show a connection between Fokker-Planck equations in non-homogeneous flows and the Brownian Configuration Fields. Most importantly, the method is used to show how this technique can be generalized to include the effects of center-of-mass diffusion of the polymer chains on stress. Such an effect might be important in relieving the prediction of stress boundary layers in finite element simulations.

Thursday 9:45 Massachusetts

**Hi fidelity coarse grained models for dynamics of dilute polymeric solutions**

Vidya Venkataramani, Radhakrishna Sureshkumar, and Bamin Khomami  
*Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States*

Fluorescence microscopy of model macromolecules, namely DNA, in a variety of flow fields has shown that multi-segment bead-rod and bead-spring descriptions are required to describe both single molecule dynamics such as molecular individuality, unraveling/tumbling dynamics as well as the rheological properties of the solution, namely, viscosity and the mean molecular extension. Motivated by this fact, we have been
involved in developing novel coarse graining strategies that contain information regarding the internal degrees of freedom of the chain as well as highly efficient mesoscopic simulation techniques for dynamics of polymeric solutions under flow. In this presentation our progress in both areas will be discussed. Specifically, the following issues will be discussed:
- Development of a reduced-order configuration-based model for dilute macromolecular solutions that relies on partitioning the phase space accessible to macromolecules into a few configuration classes, namely, folds, half dumbbells, kinks, dumbbells, coils and extended states. In turn, the evolution of the populations of the configurations are described using a population dynamics model while an evolution equation for the end-to-end vector of a configuration is written using a unique force law that is consistently derived from a multi-bead spring description. The total stress is then calculated as a sum over the contributions from the different classes weighted by their probability of occurrence. Model predictions are compared with the underlying bead-spring model in the startup of steady shear and uniaxial extension.
- The performance of the random walk spring (RWS) model for flexible linear macromolecules is evaluated using a successive fine-graining approach. Specifically, it is shown that the transient response of the fine-grained version of this model (i.e., 3-rods per spring) closely match predictions of bead-rod models at a much reduced CPU time (i.e., by a factor of 7-10).

Thursday 10:35 Massachusetts

Schmidt number effects in DPD simulation of polymer solutions
Vasileios Symeonidis¹, Bruce Caswell², and George E. Karniadakis¹
¹Division of Applied Mathematics, Brown University, Providence, RI 02912, United States; ²Division of Engineering, Brown University, Providence, RI 02912, United States

The essence of the Dissipative Particle Dynamics (DPD) model is a particulate fluid with rare-gas number densities, but with the compressibility of liquids. These properties are sufficient to yield good results for equilibrium problems, but are insufficient in dynamics. It has been known for some time that diffusion is not properly captured by the standard Velocity-Verlet scheme which is effectively confined to self-diffusion Schmidt numbers (Sc) of O(1). When Lowe's scheme is employed it is shown that Sc up to 10⁵ are easily achieved. The effect of Sc on the outcomes of several problems are examined.

Thursday 11:00 Massachusetts

Simulation of the rheology of concentrated polymer solutions by dissipative particle dynamics (DPD)
Charles W. Manke, Zeena Kas, Ildiko Macioce, and Jeffrey Potoff
Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, United States

Polymer solutions in the concentration range from 1.0 < c[η] < 10 are modeled by Dissipative Particle Dynamics (DPD) using a bead and spring model with 20 beads connected by FENE springs. The solvent is modeled by free DPD particles, and polymer-solvent thermodynamic interactions are set to provide a good solvent environment at low polymer concentration. As polymer concentration is increased, thermodynamic screening effects are evaluated by measuring the change in average radius of gyration as a function of polymer concentration. Hydrodynamic screening effects are monitored by evaluating the center-of-mass velocity autocorrelation function for a single polymer chain. We find that both thermodynamic and hydrodynamic screening effects occur as polymer concentration increases from semidilute solutions to concentrated solutions, in qualitative agreement with the known behavior of solutions of flexible chain polymers.

Thursday 11:25 Massachusetts

Transient conformational change of bead-spring ring chain during creep process
Hiroshi Watanabe
Institute for Chemical Research, Kyoto University, Uji, Kyoto 6110011, Japan

The bead-spring model is the fundamental model in the field of polymer physics but its conformational dynamics under stress-controlled conditions had not been analyzed so far. For completeness of the model, this dynamics was recently analyzed for linear and star bead-spring chains during the creep process under a constant stress. In this presentation, the analysis is extended to the bead-spring ring chain having no free end. Since all segments of the ring chain are equivalent (due to the lack of the chain end) and the orientational anisotropy summed over these segments corresponds to the stress (stress-optical rule), the segments have the same, time-independent anisotropy throughout the creep process. In other words, no retardation occurs for the segment anisotropy. However, the ring chain exhibits the retarded creep behavior (delay in achieving the steady flow state), as similar to the behavior of the linear chain. The analysis of the conformational dynamics reveals that this retardation of the ring corresponds to growth of the orientational correlation between different segments with time. The analysis also indicates a difference between the ring and linear chains that the ring segments have either positive or negative correlations depending on their separation along the chain backbone while the correlation is always positive for the segments of the linear chain.

Thursday 11:50 Massachusetts

Crosslinking of water-soluble polymers
Peter E. Clark
Chemical and Biological Engineering, University of Alabama, Tuscaloosa, AL 35487, United States

Crosslinked water-soluble polymers are used in the oilfield as fracturing fluids, temporary plugs, and pipeline pigs. They are also finding uses in controlled release drug delivery. The cross linked systems used in the oilfield are usually composed of a guar or guar derivative and borate or...
metal ions. With guar the crosslinking occurs between the crosslinker and the cis-hydroxyl groups on the polymer. Most commercial systems are engineered to be pH or in some cases temperature activated. With titanium chelaletes, the reaction rate is shear sensitive. At high shear rates, the reaction is inhibited but it will go to completion when the shear rate drops to zero. Borate crosslinked systems exhibit chaotic behavior at low shear rates when the pH is just high enough to cause weak crosslinking. As the pH is increased this behavior seems to disappear, but the gels are so viscoelastic that steady shear measurements are difficult or impossible. These are just two examples of interesting behavior exhibited by crosslinking systems. We have used a continuous mixing system coupled with a controlled stress rheometer equipped with a cone and plate fixture to study the crosslinking reaction as a function of shear rate. Using initial rate methods we found that the reaction changes order as a function of shear rate. We will present a discussion of these two observations as well as methods to easily evaluate polymer/crosslinker systems to predict their behavior under various conditions.

Thursday 12:15 Massachusetts
Disentanglement behavior of DNA solutions as probed with particle-tracking velocimetry
Pouyan E. Boukany and Shi-Qing Wang
Polymer Science, University of Akron, Akron, OH 44325, United States

We study an ideal entanglement network to test a number of emerging ideas about how topological entanglement reorganizes in presence of shear flow. Aqueous DNA solutions can be highly entangled at very low concentrations and thus very soft yet sluggish. A particle tracking velocimetric method, which was developed recently in our lab [1], was applied to determine the velocity profile of the DNA solutions in simple shear under several flow conditions including large step strain, large amplitude oscillatory shear, startup continuous shear and creep. It is shown that all of the nonlinear viscoelastic flow behavior is associated with development of inhomogeneous shear when nucleation of chain disentanglement takes place in reaction to imposed shear deformation.


Symposium MF
Microfluidics, Confined Systems and Thin Films
Organizers: Todd Squires and Nicos Martys

Thursday 8:05 Connecticut
Flow instabilities of two-phase immiscible fluids in microfluidic devices
Joo Sung Lee, Rebecca Dylla-Spears, and Susan J. Muller
Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, United States

Immiscible two-phase Newtonian flows are often used in microsystems such as microcoolers and encapsulating drops. Even in the low Reynolds number regime, flow instabilities of multiphase flow have been observed in hydrofocusing flows and diverging channels. In this study, we have derived inspiration from the experimental observation of Dreyfus et al. of various flow patterns in two-phase hydrofocusing flows [1]. To explain the origin of these instabilities, which differ from those in macroscale two-phase flows, we have investigated hydrofocusing flows using theoretical stability analysis and flow visualization in MEMS channels. The periodic wave instability was very similar to the macroscale two-phase flow independent to the entry conditions, however, the phase diagram for drop formation has no universality.


Thursday 8:30 Connecticut
Effects of geometry and fluid elasticity during polymeric droplet pinch-off in microfluidic environments
Amy Shen1, Radhakrishna Sureshkumar2, and Ben Steinhaus1
1Mechanical and Aerospace Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States; 2Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States

We investigate the effects of fluid elasticity and channel geometry on polymeric droplet pinch-off by performing systematic experiments using viscoelastic polymer solutions which possess practically shear rate-independent viscosity (Boger fluids). Four different geometric sizes (width and depth are scaled up proportionally at the ratio of 0.5, 1, 2, 20) are used to study the effect of the length scale, which in turn influences the ratio of elastic to viscous forces as well as the Rayleigh time scale associated with the interfacial instability of a cylindrical column of liquid. We observe a power law relationship between the dimensionless (scaled with respect to the Rayleigh time scale) capillary pinch-off time, T, and the elasticity number, E, defined as the ratio of the fluid relaxation time to the time scale of viscous diffusion. In general, T increases dramatically with increasing E and for E = 10, achieves values exceeding 100. Furthermore, coil-to-stretch transition effects can be inferred as the Weissenberg number, defined as the ratio of the fluid relaxation time to the inverse of the characteristic extension rate, approaches 0.5. The inhibition of "bead-on-a-string" formation is observed for flows with effective Deborah number, De, defined as the ratio of the fluid relaxation time to the Rayleigh time scale becomes greater than 10. It is shown that models that neglect the enhanced extensional viscosity of the polymer
solutions become increasingly more inaccurate as the De increases. For sufficiently large values of De, the Rayleigh instability may be modified substantially by fluid elasticity.

Thursday 8:55 Connecticut

**Stable jets of viscoelastic fluids and self-assembled cylindrical capsules by hydrodynamic focusing in microfluidic devices**

Kazem V. Edmond\(^1\), Anthony D. Dinsmore\(^1\), and Jonathan P. Rothstein\(^2\)

\(^1\)Physics, University of Massachusetts, Amherst, MA, United States; \(^2\)Mechanical and Industrial Engineering, University of Massachusetts, Amherst, MA 01003, United States

In recent years, a number of studies have investigated the use of flows developed within microfluidic devices to generate emulsions with precisely controlled droplet sizes and polydispersity. In this talk, we will present a series of microfluidic hydrodynamic flow focusing experiments designed to produce long-lived cylindrical jets of viscoelastic polymer solutions. These stable cylinders are then subsequently used as templates for the assembly of nanoparticles at the oil-water interface in order to form rigid, semi-permeable cylinders with potential applications in encapsulation and in novel structural materials. In the flow-focusing device, an aqueous solution of polyacrylamide flows coaxially with an immiscible oil, experiences a strong extensional flow over a short distance, and then flows into a uniform cylindrical tube. At sufficiently high flow rates, the aqueous phase forms a cylindrical jet with a diameter of 10–90 microns which can remain stable for several centimeters downstream. An scaling analysis will be presented to which accounts for the role of extensional rheology and first normal stress difference on the stability of the viscoelastic jets.

Thursday 9:20 Connecticut

**Physical properties of shear gel particles created using microfluidic channels**

Gordon Christopher and Shelley L. Anna

*Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

Microfluidic systems have been used to create monodisperse particles using a variety of materials. Solid particles with controlled size can be useful in biotechnology applications including protein and DNA assays and drug delivery. Here we present a method utilizing microfluidic channels to produce microparticles from an agarose shear gel. Shear gels are formed via a known process in which hot agarose solution is continuously sheared at a high rate during cooling. During this process, concentrated agarose gel microdomains become suspended in the solvent, producing a relatively homogeneous viscous liquid that exhibits a yield stress. The final properties of the shear gel depend on the shear rate, temperature profile, and initial agarose concentration. Agarose demonstrates a number of favorable properties for this application including biocompatibility and a large thermal hysteresis that allows for a stable final gel.

We create droplets of the agarose shear gel in our microchannels and subsequently re-melt the agarose by passing the droplets over an embedded aluminum heater. As the heated droplets cool in the presence of relatively low shear rates, a solid gel network forms resulting in a robust microparticle. As the shear gel is a viscous liquid at room temperature, we note that only local heating is required within the microdevice.

Bulk properties of agarose gels depend on the concentration of agarose and the gelling conditions. Here we characterize the size, shape, solvent interactions, and mechanical properties of the final microparticles as a function of shear gel properties, agarose concentration, and gelling conditions in the channel. We compare with properties of bulk gels produced at similar conditions. Finally, we examine the effect of particle microstructure on its encapsulation and release properties including the distribution of encapsulated molecules within the solidified gel network and the diffusion rate of these molecules out of the gel particles.

Thursday 9:45 Connecticut

**Bubble trains in non-Newtonian fluids**

M. Sullivan\(^1\), D. Angelescu\(^1\), and Howard A. Stone\(^2\)

\(^1\)Sclumberger-Doll Research, Cambridge, MA, United States; \(^2\)Division of Engineering and Applied Science, Harvard University, Cambridge, MA, United States

Microfluidic methods are finding many uses for making and manipulating multiphase flows. One class of such flows is periodic trains of bubbles in a viscoelastic polymer solution. For a Newtonian suspending liquid, the bubbles occupy a stable position along the channel centerline and are hydrodynamically decoupled when separated by more than the channel diameter. In polymer solutions, however, we have observed significant deviations of the bubble train behavior, such as drifting of the bubbles toward the channel walls and long range interactions leading to axial instabilities. These observations will be quantified.

Thursday 10:35 Connecticut

**Drag reduction and mixing enhancement of laminar flows in microchannels with micro-patterned ultrahydrophobic walls**

Jia Ou, Geoff Moss, and Jonathan P. Rothstein

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

A series of drag reduction experiments were performed for the flow of water in microchannels with ultrahydrophobic walls. These ultrahydrophobic surfaces have micron and nano-sized ridges and posts patterned in silica using photolithography and chemically modified to

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*The Society of Rheology 78th Annual Meeting, October 2006 75*
Thursday Morning

Effects of drag-reducing polymers on blood flow in bifurcated microchannels
Joie N. Marhefka1, Rui Zhao2, Sachin S. Velankar3, Hsin-Hua Hu4, and Marina V. Kameneva1
1Bioengineering, McGowan Institute for Regenerative Medicine, University of Pittsburgh, Pittsburgh, PA 15219, United States; 2Department of Biomedical Engineering, Carnegie Mellon University, Pittsburgh, PA, United States; 3Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States; 4Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA, United States

Blood-soluble drag-reducing polymers (DRPs) have been shown to produce significant beneficial effects on blood circulation, including an increase in tissue perfusion and tissue oxygenation and a decrease in vascular resistance, when injected in blood at minute concentrations. Elucidation of the mechanisms of the observed DRP effects on blood circulation is extremely important for future clinical applications of these polymers. We studied the effects of DRPs (polyethylene oxide WSR-301 and an aloe derived polysaccharide) on the microflow of red blood cell (RBC) suspensions in straight and bifurcated microchannels to test the hypothesis that DRPs cause a reduction of the near-wall cell-free layer in microvessels attenuating the "plasma skimming" effect and increasing the number of RBCs (hematocrit) entering vessel branches and capillaries. Channels used in our study include a 100 micron straight microchannel and a 100 micron channel with a series of 90° bifurcations ranging from 25 to 100 microns. Standard photolithography techniques and replica molding were used to fabricate bifurcated microchannels in polydimethyl siloxane. The channels were perfused with bovine RBC suspensions containing either 0 (control) or 0.01 mg/ml of DRP, and samples were collected from each outlet for hematocrit measurements. The outlet hematocrit values were compared to each other and to the inlet value in both DRP and control samples in order to determine whether the DRPs are attenuating the plasma skimming effect. As the RBCs flowed through the microchannels, their flow behavior was recorded with a microscopic flow imaging system. These studies clearly demonstrated that the DRPs promoted movement of RBCs closer to the vessel walls and increased concentration of RBCs in smaller channel branches. In vivo, this effect may facilitate gas transport and increase wall shear stress potentially promoting vasodilation and decreasing vascular resistance in the microvessels.

Microfluidic device for measuring red blood cell (RBC) deformability under the extensional flow
Sung Sik Lee1, Yoonjae Yim1, Joung Sook Hong2, Kyung Hyun Ahn1, and Seung Jong Lee1
1School of Chemical and Biological Engineering, Seoul National University, Seoul, Republic of Korea; 2Applied Rheology Center, Korea University, Seoul, Republic of Korea

The red blood cell (RBC) deformability has been exploited as one of the clinical diagnosis methods for specific diseases. Though the flow types used in deformability measurements are combination of shear and extensional flow, most of studies dealt with RBCs under simple shear flow. This study was undertaken to investigate the response of RBCs under the extensional flow using a hyperbolic converging microchannel. The extensional strain rate (velocity gradient) at the center of the channel was calculated by computer simulation (Fluent 6.1). Microchannels were fabricated by molding polydimethylsiloxane (PDMS). The microchannel attached to slide glass was spin-coated with PDMS so that the microfluidic device was manufactured to have 4 PDMS walls. RBCs were suspended in polyvinyl pyrolidone (PVP) solution to facilitate deformation more easily. Elongational Index (EI) was defined for quantification; EI= (A-B)/(A+B) where A and B are the vertical and horizontal lengths of the fitted ellipse. As we increase the input flow rate of PVP-RBC suspension (Q=1 ~40µl/min), RBCs were deformed by extension flow at hyperbolic region and EI increased. EI was saturated at the specific stress about 0.5-0.6 which is comparable to that obtained from shear flow. However, at low stress region, EI under extensional flow was larger than that of shear flow. From those results, we postulate that RBC deformation mechanisms are different in simple and extensional flows. This will be true in complex flow field as well.

Deformability-based analysis of red blood cells flowing in microchannels
Giovanna Tomaiuolo, Marino Simeone, and Stefano Guido
Dipartimento di Ingegneria chimica, Università di Napoli Federico II, Napoli 80125, Italy

The deformability of red blood cells flowing in microvessels is essential to maintain optimal blood circulation and to allow gas transfer between blood and tissues. From a pathological viewpoint, reduced RBC deformability is involved in a number of blood diseases, such as Thalassemia, Iron Deficiency, Congenital Spherocytic and Non Spherocytic Anemias, Idiopathic Myelofibrosis. In spite of such physiopathological relevance, measurements of RBC deformability are usually of difficult clinical application, being still carried out by approximate methods and under conditions quite different from those occurring in vivo. In this work, we investigate RBC deformability in microcapillaries having size similar to...
that of the cells. The velocity and shape of flowing RBCs is investigated by an inverted microscope equipped with a CCD camera and a motorized x-y stage and focus. Experimental variables include flow rate and size and length of microcapillaries. RBCs both from healthy donors and from patients have been investigated and compared.

Thursday 12:15 Connecticut

Shear banding of polymer blends
Angelo Ferrara, Sergio Caserta, Marino Simeone, and Stefano Guido

Dipartimento di Ingegneria chimica, Università di Napoli Federico II, Napoli 80125, Italy

The deformation of droplets in confined geometries has recently received much attention in the literature, especially in view of possible microfluidics applications. In such situations, wall effects play a significant role on flow-induced drop deformation. In this work, the morphology evolution of a model polymer blend undergoing shear flow in a translating parallel plate device is investigated. We found that in a range of experimental conditions a flow-induced transition from a homogeneous drop distribution to the formation of bands parallel to the flow direction takes place. The kinetics of this phenomenon is investigated as a function of viscosity ratio, shear rate and gap thickness. The drop size distribution within the bands and the velocity profile are also studied.

Symposium GP
General Papers

Organizers: Jason Butler and Phil Sullivan

Thursday 8:05 Rhode Island

Rheology of polymer/clay nanocomposites
Michail K. Dolgovskij1, Christopher W. Macosko1, and Jan Vermant2

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Melt rheology has been used as a powerful tool in assessing the state of dispersion in polymer/clay nanocomposites. The terminal region of the elastic modulus undergoes a transition from liquid-like to solid-like behavior when the clay disperses into a "house of cards" type network. Both polystyrene (PS) and polypropylene (PP) nanocomposites were prepared by melt blending. Rheological data from the dispersed system were considered with scaling laws for flocculated systems and a fractal dimension was determined for the nanocomposite materials. The fractal dimension was used as a measure of the openness or closeness of the clay network structure in the melt. Fractal dimensions determined from X-ray scattering experiments were used to validate our analysis. Additionally, percolation theory was applied to determine an average aspect ratio for clay particles in our systems.

Thursday 8:30 Rhode Island

Quiescent and flow-induced crystallization of polypropylene-clay nanocomposites
Mark A. Treece and James P. Oberhauser

Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, United States

While strong deformations are known to promote homogeneous nucleation in semi-crystalline polymers, inorganic filler is frequently added as a heterogeneous nucleating agent in commercial processing. Recently, organically modified montmorillonite clay has seen extensive use in the synthesis of polymer-clay nanocomposites (PCNs), where the successful exfoliation and dispersion of the clay has led to significant property enhancement at low volume fraction. However, the influence of these anisotropic, nanoscale fillers on crystallization kinetics and morphology, particularly following a deformation, has been largely ignored.

This work investigates the quiescent and flow-induced crystallization of polypropylene (PP)-clay nanocomposites. A commercial PP resin is melt-blended with 1, 3 and 5 wt% organoclay in a twin-screw extruder. Since PP has unfavorable interactions with the organoclay, additional samples are prepared with a 3:1 ratio of maleic-anhydride functionalized PP compatibilizer to organoclay.

Quiescent crystallization kinetics are quantified using isothermal and non-isothermal differential scanning calorimetry (DSC), and optical microscopy (OM) is utilized to examine the growth rate and nucleation density of each nanocomposite. Flow-induced crystallization studies are performed in a mini-extruder inspired by the designs of Janeschitz-Kriegl and Kornfield. The mini-extruder imposes a finite shear pulse, effectively decoupling the influence of melt distortion on crystallization from the tendency of flow to orient crystallites as they form. Using in situ measures of turbidity and birefringence and ex situ transmission electron microscopy (TEM) and polarizing optical microscopy (OM) analysis, we examine the effect of organoclay concentration, orientation, and dispersion on crystallization kinetics and morphology. Results suggest that the flow-alignment of clay domains strongly enhances nucleation and growth.
Dynamic rheology of thermoplastic elastomer gels derived from poly[styrene-\text{-}b\text{-}(ethylene-\text{-}co\text{-}butylene)-\text{-}b\text{-}styrene] triblock copolymers and aliphatic oils

Ravi Shankar1, Saad A. Khan2, Rudolf R. Bukovnik3, Tushar K. Ghosh4, and Richard J. Spontak1

1Department of Materials Science & Engineering, North Carolina State University, Raleigh, NC 27695, United States; 2Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905, United States; 3Tyco Electronics Corporation, Fuquay-Varina, NC 27526, United States; 4Fiber & Polymer Science Program, North Carolina State University, Raleigh, NC 27695, United States

Thermoplastic elastomer gels (TPEGs) are generally composed of multiblock thermoplastic elastomers wherein the rubbery blocks are swollen by a selective solvent. In this work, a linear poly[styrene-\text{-}b\text{-}(ethylene-\text{-}co\text{-}butylene)-\text{-}b\text{-}styrene] (SEBS) triblock copolymer is swollen with an aliphatic-rich mineral oil (503 Da) or one of three \(\alpha\)-olefins with molecular weights ranging from 287 to 1400 Da. Three series of TPEG formulations possessing SEBS copolymers differing in molecular weight and copolymer concentrations varying from 5 to 30 wt% have been prepared and examined by dynamic rheology performed at temperatures ranging from 25\(^\circ\)C to 150\(^\circ\)C. 

Solvent driven gelation and melting of poly(vinyl alcohol) hydrogels

Gavin J. Braithwaite\(^1\) and Norma Turner\(^2\)

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Poly(vinyl alcohol) (PVA) hydrogels are being increasingly considered for use in biological applications due to their high hydrophilicity and excellent biocompatibility. Traditionally, these hydrogels have been manufactured using a freeze-thaw process which is thought to physically drive the PVA chains together during the freezing process. This freezing forces a phase separation which subsequently allows physical crosslinking through hydrogen-bonding upon thawing. However, it has recently been noted [1] that solvent quality can be used to manipulate the phase behavior of the polymer solution. If the solution conditions are right the gelation process of the hydrogel can be controlled, allowing manipulation of the gelation and working times, and the final properties.

Viscoelastic properties of blood in evaluation of sub-lethal damage to RBCs in blood-contacting devices

Philip J. Marascalco\(^1\), Sean P. Ritchie\(^2\), Trevor A. Snyder\(^2\), and Marina V. Kameneva\(^1\)

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The measurement of plasma-free hemoglobin is a standard practice in the testing of the biocompatibility of blood contacting devices such as ventricular assist devices, dialysis machines, and cardiopulmonary-bypass circuits for the assessment of red blood cell (RBC) damage (hemolysis). Results of these in vitro and in vivo tests provide assessment of blood trauma only. However, sub-lethal damage may exist which can cause changes in RBC mechanical properties such as a reduction in their deformability which may lead to microcirculatory impairment and shortened cell lifespan. In the present work, we investigated the applicability of measuring viscoelasticity of bovine, ovine and porcine whole blood for the evaluation of sublethal damage to RBCs. An increase in blood viscosity and elasticity without changes in hematocrit and plasma viscosity would signify a decrease in RBC deformability. Blood viscoelasticity was assessed using a Vilastic Scientific viscoelastometer with an oscillatory flow generated at a constant frequency (2 Hz) in a capillary tube. Due to the natural absence of RBC aggregation and small RBC size in normal bovine and ovine blood, viscoelastic properties are not well pronounced. However, we found that adjustment of blood hematocrit to a
standard level of 40-50% allows for the sensitive assessment of viscoelasticity in these blood types and a demonstration of a pronounced non-Newtonian behavior. Both viscosity and elasticity were found to be elevated after blood exposure to a uniform mechanical stress. Thermally rigidified RBCs demonstrated a loss of their viscoelasticity dependence on shear rate. This study demonstrated that the measurements of blood viscoelasticity can be meaningful in bovine and ovine blood. It also suggests that the shear thinning behavior seen in these blood types is mostly due to RBC deformability. Finally, this study showed that tests of blood viscoelasticity can be used for the evaluation of sublethal blood damage in vitro and in vivo trials of blood contacting devices.

Thursday 10:35 Rhode Island

**Mechanical, optical and thermal conductivity measurements on a cross-linked polybutadiene in uniaxial elongation**

David C. Venerus and Dimitre N. Kolev

*Chemical Engineering, Illinois Institute of Technology, Chicago, IL, United States*

Cross-linked elastomers have numerous applications including automobiles, sporting goods, and biomedical devices. During both their processing and application, these materials experience large mechanical stresses and thermal gradients. In this study, we investigate the mechanical, optical and thermal transport behavior of a well-defined, cross-linked polybutadiene. This material has been prepared by cross-linking a well-entangled and nearly mono-disperse polybutadiene using an organic peroxide cross-linking agent at low concentration. We report linear viscoelastic measurements of this system at various stages of cross-linking. Samples obtained after nearly complete conversion of the cross-linking agent, which can be characterized as lightly cross-linked (i.e., more than 10 entanglements per cross-link), were subjected to a series of large strain, uniaxial deformations. Measurements of the tensile stress, birefringence and two components of the thermal conductivity tensor will be reported as a function of elongation. These data are also used to examine the stress-optic and stress-thermal rules.

Thursday 11:00 Rhode Island

**Stress birefringence patterns and microstructure in strong extensional flows: Multiscale modeling and flow visualizations of long-chain branched polyethylenes**

D. Harley Klein¹, Tom C. McLeish¹, Oliver G. Harlen², David G. Hassell³, and Malcolm R. Mackley³

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It is well known that the rheology of melts of high molecular weight polyolefins is critically dependent on the branching topology, i.e., the degree of branching and the nature of the branching structure. The most notable manifestations of this dependency are the degree of strain hardening in extensional flow and the molecular weight dependence of the shear viscosity. The branching topology is dependent on the method of synthesis, with, for example, metallocene-synthesized polymers having a quite different branching structure to low-density polyethylenes. These differences can be seen in the qualitatively different stress birefringence patterns observed in strong extensional flows such as the cross-slot flow and contraction-expansion flows for polymers with different branching structures. The multi-mode pompom model proposed by McLeish and Larson contains direct information on the branching distribution, so that in fitting the rheology it should provide a link between the microstructure and the observed stress patterns. To test this, we study a series of prototype industrial polyethylenes with branching structures varying from linear to lightly long-chain-branched to highly branched. Experimental birefringence observation obtained using the Cambridge MultiPass Rheometer are compared to the numerical prediction obtained for the multi-mode pompom model obtained using the Lagrangian-based finite-element computational tool *flowSolve*.

Thursday 11:25 Rhode Island

**A molecular dynamics study of the stress-optical behavior of a linear short-chain polyethylene melt under shear**

Chunggi Baig, Brian J. Edwards, and David J. Keffer

*University of Tennessee, Knoxville, TN, United States*

In this study, we present details of the stress-optical behavior of a linear polyethylene melt under shear using a realistic potential model. We demonstrate the existence of the critical shear stress, above which the stress-optical rule (SOR) begins to be invalid. The critical shear stress of the SOR of this melt turns out to be 5.5 MPa, which is fairly higher than 3.2 MPa at which shear thinning starts, indicating that the SOR is valid up to a point well beyond the incipient point of shear thinning. Furthermore, contrary to conventional wisdom, the breakdown of the SOR turns out not to be correlated with the saturation of chain extension and orientation: it occurs at shear rates well before maximum chain extension is obtained. In addition to the stress and birefringence tensors, we also compare two important coarse-grained second-rank tensors, the conformation and orientation tensors. The birefringence, conformation, and orientation tensors display nonlinear relationships to each other at high values of the shear stress, and the deviation from linearity begins at approximately the critical shear stress for breakdown of the SOR.
Modeling reactive displacements along plane channels

Kerstin Wielage\(^1\), James J. Feng\(^2\), and Ian A. Frigaard\(^1\)

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We present results of a numerical study on the displacement of one generalized Newtonian fluid by another in a plane channel. In primary cementing of oil wells, drilling mud is displaced first by a spacer fluid and then by a cement slurry, along a narrow eccentric annulus. Here we consider a radial slice of the narrow annulus and look at a fully 2-dimensional plane channel displacement flow. In long horizontal wells, these displacement flows are typically laminar (low-moderate Re), density differences are avoided, and therefore fluid rheology plays a major role in whether or not the displacement will be effective.

In the above context we study whether it is possible to achieve enhanced displacement efficiencies by generating larger viscosities local to the interface (e.g. via some form of chemical reaction). We concentrate on the case of immiscible fluids using the diffuse interface method. The displacement efficiency depends on the contact line motion and the velocity of the finger tip. Therefore the effects of the model parameters, contained dimensionlessly in the Peclet, Capillary and Cahn numbers, are examined with respect to these two velocities.

It is well-known that high viscosity fluids generally displace lower viscosity fluids quite well. However, higher viscosities lead to higher frictional pressures, which is not acceptable for long horizontal wells. To exploit the good displacement properties of high viscosity fluids but maintain low frictional pressures over the majority of the channel, we consider displacements with low viscosity fluids that have a high interfacial viscosity, i.e. the viscosity varies non-monotonically between the viscosity of the 2 fluids. We show that this idea does actually result in higher displacement efficiencies due to the high-viscosity interfacial layer.

Thermoforming cones and cups

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Analytical solutions are given for Newtonian free forming of a sphere and Newtonian constrained forming of a cone. These cases begin with a thin, uniform polymeric sheet. The solutions for thickness, stress and manufacturing times are given for spherical free-forming and conical constrained forming, in terms of geometry and material constants. Furthermore, plug assist corrections are calculated for the constrained forming of a cone using previous research by Williams [1]. These equations are directly useful for nearly Newtonian materials such as polyester, and also for benchmarking numerical simulation code.

We will also report on Polyflow simulations of thermoforming of truncated polypropylene cups. For this we employ a nonlinear viscoelastic model (the Wagner equation) to explore the role of rheology in thermoforming. Predicted cup shapes match the measured ones.

Non-contact measurement and control of the upper platen on a combined motor and transducer rheometer
Aadil Elmoumni\textsuperscript{1} and Aly J. Franck\textsuperscript{2}
\textit{TA Instruments - Waters LLC, New Castle, DE 19720, United States;} \textsuperscript{2} \textit{TA Instruments, Alzenau, Germany}

The temperature measurement and control of the upper (rotating) platen on a Combined Motor and Transducer (CMT) rheometer has always been problematic. For temperature control systems that completely surround the sample and both measurement platens [e.g. convection ovens or concentric cylinder jackets] the measurement of temperature in the lower (stationary) platen is sufficient for both system control and accurate survey of the sample temperature. This approach is also suitable for temperature systems that control and measure the temperature of just the lower platen [e.g. Peltier or electrically heated plates] if the test temperature is close to ambient. But the further the test temperature is from ambient, the greater the chance of undesirable temperature gradients occurring within the sample. To overcome these gradients, independent control and measurement of the upper platen temperature is highly desirable. Mechanical contact to the rotating platen is not an option, as this would impact the application and measurement of torque. Previous to the introduction of this new technology [US Patent 6,931,915] the upper platen temperature could only be inferred by time-consuming calibration. Now with a temperature probe mounted directly in the upper rotating platen, whose output is read without mechanical contact, the actual platen temperature can both be measured and controlled. Rheological measurements on polymer melts will be used to show the performance for this new non-contact temperature sensor when used in conjunction with electrically heated lower and upper plates.

The AR-G2 magnetic bearing rheometer with a Du Noüy ring for interfacial rheological measurements
Aly J. Franck\textsuperscript{1} and Bernard Costello\textsuperscript{2}
\textit{TA Instruments, Alzenau, Germany;} \textsuperscript{2} \textit{TA Instruments, Crawley, United Kingdom}

A number of methods have been developed over the years to investigate the surface and interfacial shear rheology. The Du Noüy ring, commonly used for interfacial tension measurements has been successfully applied to interfacial shear testing. Like the bi-cone, the ring is located at the interface of two liquids or a liquid and a gas. When the ring is subjected to an angular displacement, the surface between the ring and the circular wall of the vessel containing the liquids is sheared. The light construction of the ring permits the characterization of very fragile interfaces, without the inertia dominating the experiment. However, most bulk rheometers have too low sensitivity and too high inertia to use the Du Noüy ring in oscillation mode. The AR-G2 rotational rheometer with a torque range of almost nine decades and sensitivity comparable to that of the specialized interfacial rheometers, has been successfully used in conjunction with a Du Noüy ring to perform dynamic interfacial rheology measurements over and beyond the range of specialized instruments. The Du Noüy ring is attached to the stress motor, mounted on the rheometer slide. In the basic setup, a circular glass dish locates in the center on the Peltier plate and is held in position with an annular Peltier cover. The geometry is treated as a two dimensional analogue of the concentric cylinder system.

The adsorption of lysozyme, a protein isolated from egg white was monitored at the water-decane interface. After the adsorption of the native globular protein at the interface partial unfolding, exposing the hydrophobic groups takes place. The proteins aggregate and form an elastic layer. The continuous increase of the interfacial shear modulus suggest that proteins continue to unfold and aggregate, forming multi-layers at the interface.

The specification of controlled torque rheometers
Bernard Costello\textsuperscript{1}, Raoul E. Smith\textsuperscript{2}, Russell Ulbrich\textsuperscript{2}, and Aly J. Franck\textsuperscript{3}
\textit{TA Instrument, Crawley RH10 9NB, United Kingdom;} \textsuperscript{2} \textit{TA Instruments, New Castle, DE 19720, United States;} \textsuperscript{3} \textit{TA Instruments, Alzenau, Germany}

Manufacturers of scientific instruments describe the performance of their products by means of a set of specifications. These specifications are often used as the basis of comparison between instruments, but for controlled torque rheometers, no generally accepted way of arriving at them exists. For example, we show here that the “minimum torque” can be defined in many ways; it is possible to produce figures that differ by several orders of magnitude. This is an unsatisfactory situation, since it makes any comparison between instruments problematical. In other industries the difficulty does not arise. The specifications for analytical balances or voltmeters, for example, are clearly defined. Controlled torque rheometers are generally more sophisticated than balances or voltmeters, but we argue here that definitions can be arrived at for
rheometers that allow all manufacturers to describe the full potential of their instruments, while providing a sound basis of comparison for prospective purchasers. We propose these definitions to the Society of Rheology in the hope that they may lead to a universally accepted methodology for the specification of rheometer specification.

Wednesday  6:10  Casco Bay Exhibit Hall  PO4
A study of the rheological properties and droplet size distributions of some common nasal decongestant spray formulations
Mark Bumiller and Philip Rolfe
Malvern Instruments, Southborough, MA, United States

Rheological characterization is a powerful tool in the formulation of sprays where specific droplet sizes are required. This poster presents both a basic approach to model droplet behavior as a function of rheological properties and experimental data from multiple characterization techniques including rheology, laser diffraction and image analysis. The droplet size distribution obtained from the nasal pump is a function of factors ranging from actuation characteristics, pump design to the rheological properties of the formulation liquid. In particular microcrystalline cellulose and carboxymethylcellulose (CMC) is used as a viscosity modifier to enhance the residence time in the nasal cavity. Results indicate that the long relaxation time described by the low frequency storage modulus \( G' \) that relates to the extensional rheological behavior of the material.

Wednesday  6:10  Casco Bay Exhibit Hall  PO6
Rheology of heterogeneous polymer melts
Chuck L. Rohn\(^1\), Philip P. Rolfe\(^2\), and Eric Bennett\(^3\)
\(^1\)Rheology, Malvern Instruments, Inc., Bridgewater, NJ 08807, United States; \(^2\)Rheology, Malvern Instruments, Inc., Southborough, MA 01772, United States; \(^3\)Malvern Instruments, Southborough, MA, United States

The rheology of heterogeneous polymer melts, such as alloys, polyblends, and fiber filled plastics can not be treaded as simple, homogeneous melt. In order to understand these data appropriate for plastic processing, machine design, and modeling, both capillary and rotational rheometers are needed. Presented is pressure flow (capillary) and drag flow (rotational) of the rheology of two polymer systems: a fiber filled engineering plastic and polyblend. Linear and non-linear viscoelastic tests are performed. The effect of shear history and of flow induced fiber orientation from capillary pressure flow is compared with rotational data. The Cox-Merz relationship, strain recovery, die swell, time temperature superposition is discussed.

Wednesday  6:10  Casco Bay Exhibit Hall  PO7
Rheological measurements on fresh building materials
Michael Haist\(^1\), Harald S. Müller\(^1\), Cornelia Küchenmeister\(^2\), and Jint Nijman\(^3\)
\(^1\)University of Karlsruhe, Karlsruhe 76128, Germany; \(^2\)Rheology, Malvern Instruments, Inc., Bridgewater, NJ 08807, United States; \(^3\)Malvern Instruments, Southborough, MA, United States

Fresh building materials, such as cementitious pastes, grouts or concrete can be characterized as suspensions containing particles ranging from approximately 0.3 micrometer up to several millimeters in diameter. These suspensions are normally highly filled with phase-contents up to 60 vol.%. The rheological properties of such systems are therefore strongly affected by the granulometric properties of the particles as well as by organical chemical admixtures, which are generally used in order to modify the rheological properties of such systems. As the properties of building materials at the hardened state are strongly affected by the workability in the fresh state, the measurement and control of the rheological properties of such materials is of great interest.

Measuring the rheological properties of building materials is generally afflicted with various problems such as sedimentation, shear induced segregation and/or slippage. Therefore standard measurement techniques using plate-plate geometries etc. cannot be used. Before this background a new measuring cell for the HAAKE MARS rheometer was developed at the University of Karlsruhe in cooperation with Thermo Electron. The measurement cell consists of cylindrical cup of a special design and a vane-like sensor. In order to prevent wall-slippage, the wall of the cylindrical cup is equipped with axial slits which are evenly distributed over the circumference of the cup. Different sized metal strips can be mounted into these slits to create a variable serration of the inner wall of the cup. The special flexible design of the measurement cell allows for an easy adaption of the cell to a wide range of different samples. Large test-series were performed to prove that wall-slippage and segregation can be completely prevented using the new measurement cell.

Wednesday  6:10  Casco Bay Exhibit Hall  PO8
Determination of the mechanical properties of a PVC coated wire with a new clamping fixture for rotational rheometers
Jint Nijman\(^1\) and Jan P. Plog\(^2\)
\(^1\)Thermo Electron Corporation, Karlsruhe 76227, Germany; \(^2\)Thermo Electron Corporation, Newington, NH 03801, United States

The dynamic mechanical properties of a PVC coated wire, as used in electrical wiring, have been measured using a new solids clamping fixture for the HAAKE MARS rheometer. This fixture can be used for a wide range of solid and semi-solid materials. It provides self-centering and automatic clamping force adaptation for the sample as well as a very simple semi-automatic gap adjustment for a wide range of sample
thicknesses with just one fixture. For studying the effect of the degradation of the plasticizer in the PVC coating material, the dynamic mechanical properties of a series of wire samples were measured in the temperature range of -100 °C to 200 °C. The individual samples differed in the way they were subjected to heat treatments before the measurement.

**Wednesday 6:10 Casco Bay Exhibit Hall**

**New and improved devices for measuring Electro- (ERF) and Magneto Rheological Fluids (MRF)**

Joerg Laeuger and Patrick Heyer  
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Magneto-rheological (MRF) and Electro-rheological Fluids (ERF) are functional fluids, which change their rheological behavior after a magnetic or an electric field is applied, respectively. In recent years large improvements in the stability and the performance of MRFs and ERFs led to an increasing number of practical applications of these fluids, ranging from dampers and clutches for automobiles, to earthquake protection of bridges and houses, and to haptic devices for medical surgery. However, in order to theoretically understand the complex behavior of these fluids and to tailor the fluids and the devices to the specific application, advanced and flexible testing capabilities are needed. To achieve this goal magneto- (MRD) and electro-rheological devices (ERD) have been designed. The MRD, which can be temperature controlled by a circulating liquid, is build around a parallel-plate measuring geometry. Maximum magnetic flux densities of up to 1 Tesla in the air gap between the two plates are possible. The homogeneity of the magnetic field inside the MRD, i.e. the magnetic flux density at the sample's location, has been validated with a three-dimensional Hall sensor. Two different ERD system, both temperature controlled by Peltier elements, were designed based on a cylinder measuring system and a parallel-plate geometry, respectively. In both systems a voltage of up to 12.5 kV can be applied to the rotating bob or upper plate, whereas the cup or the lower plate are grounded. The MRD as well as the ERD systems are accessories to the Physica MCR Rheometer from Anton Paar. It is possible to use all rheological test modes of the rheometer simultaneously to the software controlled setting of well defined magnetic or electric fields. The working principle and the performance characteristics of the devices as well as yield stress and flow curve results are shown. In addition oscillatory testing, which give information on the visco-elastic behavior of these fluids at various filed strengths, are presented.

**Wednesday 6:10 Casco Bay Exhibit Hall**

**A comparison of extensional rheometers for polymer solutions**

Ross Clark¹, Maarten van der Wielen², Nancy Henderson³, and George Thurston³  
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Extensional viscosity is an important but difficult to measure attribute of water soluble polymer solutions. For this study, three different extensional rheometers are compared to each other using common water soluble polymer solutions. The Haake CaBER (capillary breakup), Vilastic (dynamic contraction flow) and Rheometrics RFX (opposed jet stagnation point) represent 3 different approaches to measuring extensional viscosity. Our testing shows that these diverse instruments are capable of relative agreement in ranking samples but have little overlap with respect to viscosity range. The RFX can measure over the widest viscosity range and still represents an excellent way to collect extensional viscosity data. The CaBER is an interesting instrument that functions best with samples of moderately high viscosity with a relatively high Trouton ratio. The Vilastic is unique in providing both extensional viscosity and elasticity information. Its range is limited to fairly thin fluids and Trouton ratios of > 3. Measurement with sugar, xanthan, cellulose gum and synthetic thickeners shows that all instruments can discern between simple fluids like sugar and polymer solutions. Furthermore, differences due to molecular weight and polymer environment are ranked correctly with each instrument. In each case, the lower molecular weight polymer was found to have a lower Trouton ratio, as expected. When xanthan gum was placed in a salt containing system the Trouton ratio decreased due to stiffening of the molecule, also as expected.

**Wednesday 6:10 Casco Bay Exhibit Hall**

**An end users experience with the CaBER for water soluble polymers**

Maarten van der Wielen  
*Nijmegen R&D, CP Kelco, Nijmegen NL-6500 AA, The Netherlands*

Extensional viscosity is a key variable in many common processes. Coating, spraying, pumping and even swallowing all have an extensional component. Recently, a commercial instrument using the CaBER (capillary break-up elongational rheometry) technique has been introduced to measure these important properties. While the theory of the CaBER technique has been analyzed in depth and some experimental data published, these investigations tended to focus on idealized polymers. The area of industrial water soluble carbohydrates has not been well explored by the CaBER. Our operational experience with such systems will be described and discussed. Several cellulose gum (sodium carboxymethyl cellulose) solutions (all polydisperse) were evaluated for shear and extensional properties. The samples varied in molecular structure (either weight-average molar mass and/or distribution of chemical groups) and concentration. It is known that these variations will result in different performance in applications. Conformational changes as caused by e.g. addition of salt will also cause a change in performance as the charges on the polymer are screened. The measurement protocol for the CaBER can be varied with respect to amount of plate separation, rate of movement and profile of the movement. All of these effect the filament produced and thus the final extensional strain and strain rate. Our practical experience with this technique should be useful for other investigators as they begin to probe industrial systems with this methodology. An improper choice of conditions can result in poor quality data or even no data at all.
commercial organoclays, Cloisite exhibit a solid-like response at low applied stress followed by yielding above an apparent yield stress. The presence of free surfactant is shown by xylene and subjected to oscillatory and steady shear experiments in a controlled-stress rheometer. Experimental data show that all dispersions exchange reaction in our laboratory, yielding a broader range of surfactant surface coverage. The resulting organoclays were dispersed in p-xylene and subjected to oscillatory and steady shear experiments in a controlled-stress rheometer. Additional organoclay samples were prepared by performing the cation exchange reaction in our laboratory, yielding a broader range of surfactant surface coverage. The resulting organoclays were dispersed in p-xylene and subjected to oscillatory and steady shear experiments in a controlled-stress rheometer. Experimental data show that all dispersions exhibit a solid-like response at low applied stress followed by yielding above an apparent yield stress. The presence of free surfactant is shown to significantly weaken the organoclay network, while a modest increases in surfactant surface coverage leads to a considerably more solid-like dispersion. A novel wet scanning electron microscopy technique provides direct imaging of the mesoscale structure responsible for changes in solid-like rheology and yield behavior.

Wednesday 6:10 Casco Bay Exhibit Hall

Experimental rheophysical investigation on concentrated noncolloidal particle suspensions in a wide-gap Couette cell
Sébastien Wiederseining and Christophe Ancey
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An optical visualization apparatus has been developed to measure the particle velocity and concentration profiles of highly concentrated particle suspensions in a Couette rheometer. When studying rheological properties of particle suspensions, experimentalists are faced with a number of issues resulting from the presence of particles. For many noncolloidal particle suspensions, the typical particle size is large relative to the standard rheometer gap. In practice, to avoid finite-size effect, a classical approach involves using large-sized geometries, e.g., wide-gap Couette cells.

For this kind of geometry, the flow curve must be derived by solving the so-called Couette inverse problem, which stays a difficult topic despite many attempts. We have recently developed a specific method based on wavelet decomposition [J. Rheol. 49 (2005) 441-460]. An alternative way of obtaining the flow curve is to measure the velocity profile across the gap, then differentiate it to derive the shear rate. We carried out experiments to compare the two methods. Experimental investigations were conducted on iso-index, iso-density suspensions made up of PMMA particles within an Newtonian fluid. The velocity profile was measured using Fluorescent Particle Imaging Velocimetry techniques. Other processes (wall slipping, particle depletion or migration, and shear localization) are also documented with this technique. We present our preliminary results.

Wednesday 6:10 Casco Bay Exhibit Hall

Processing of polypropylene-clay nanocomposites: Single-screw extrusion with in-line supercritical carbon dioxide feed versus twin-screw extrusion
Mark A. Treece and James P. Oberhauser
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This work investigates two different melt-blending strategies for preparing compatibilized polypropylene-clay nanocomposites, specifically: (1) conventional twin-screw extrusion, and (2) single-screw extrusion capable of direct supercritical carbon dioxide (scCO2) feed to the extruder barrel. Proportional amounts (3:1) of maleic anhydride functionalized polypropylene compatibilizer and organically modified montmorillonite clay at clay loadings of 1, 3, and 5 wt% are melt-blended with a polypropylene homopolymer using the two approaches. The basal spacing, degree of exfoliation, and dispersion of organoclay is assessed using X-ray diffraction, transmission electron microscopy, and rheology. In terms of the latter, both steady shear and small-amplitude oscillatory shear provide information about the apparent yield stress and solid-like terminal behavior respectively. Finally, nanoindentation is performed to determine the room temperature modulus of each melt-blended nanocomposite. The results reveal unequivocally that the high shear of the twin-screw process is vastly superior to the single-screw with in-line scCO2 addition in generating well-exfoliated, percolated polypropylene-clay nanocomposites. It is likely that increased contact time between clay and scCO2 is necessary for scCO2 to positively affect exfoliation.

Wednesday 6:10 Casco Bay Exhibit Hall

Rheology and microstructure of organoclay dispersions
Jin Li and James P. Oberhauser
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Over the past decade, polymer-clay nanocomposites (PCNs) have attracted intense research and commercial interest due to profound improvements in material properties achieved with only modest clay loading. One such clay is montmorillonite, which consists of layered planar silicates approximately 1 nm thick and 400 - 1,000 nm long separated by a van der Waals interlayer. Through the addition of surfactant, the interlayer may be rendered organophilic via a cation exchange process, yielding so-called organoclays.

This work uses mechanical rheology to probe the solid-like network formed in organoclay dispersions. Some dispersions are based upon two commercial organoclays, Cloisite® 15A and 20A, which differ in the quantity of surfactant used in the cation exchange reaction. In both cases, the amount of surfactant is in excess of the cation exchange capacity of montmorillonite. Removal of unexchanged free surfactant and subsequent thermogravimetric analysis demonstrates that the as-received, unexchanged and surfactant extracted organoclays possess different levels of free surfactant and grafted surfactant surface coverage. Additional organoclay samples were prepared by performing the cation exchange reaction in our laboratory, yielding a broader range of surfactant surface coverage. The resulting organoclays were dispersed in p-xylene and subjected to oscillatory and steady shear experiments in a controlled-stress rheometer. Experimental data show that all dispersions exhibit a solid-like response at low applied stress followed by yielding above an apparent yield stress. The presence of free surfactant is shown to significantly weaken the organoclay network, while a modest increases in surfactant surface coverage leads to a considerably more solid-like dispersion. A novel wet scanning electron microscopy technique provides direct imaging of the mesoscale structure responsible for changes in solid-like rheology and yield behavior.

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The Society of Rheology 78th Annual Meeting, October 2006
Flow-SAXS studies of silica nanoparticles in polymer solutions
Frank Snijkers and Jan Vermant
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The changes in the microstructure, induced by shear flow, of silica nanoparticles in aqueous polymer solutions were investigated by synchrotron X-ray scattering. Ludox-TM50 particles were dispersed in solutions of hydroxypropylcellulose in water and polyethyleneoxide in water, respectively. Volume fractions ranged from 0.01 to 0.2. Polymer concentrations and molecular weights were also varied. The dispersions were subjected to steady state shearing flow in a Couette shear cell, mounted onto a SAXS beamline at the European Synchrotron Radiation Facility (BM26, DUBBLE). The 2D scattering patterns were recorded and the anisotropy was analyzed by using an expansion of the structure factor into spherical harmonics. At low deformation rates, the scattering patterns suggested the presence of a weak particle network, caused either by...
bridging or depletion. The anisotropy of the scattering pattern reflected a structure predominantly oriented in the vorticity direction. At higher shear rates, the anisotropy was reversed and a flow oriented structure was obtained. For the silica-polyethyleneoxide solution composites, pronounced particle necklaces ('strings') were observed to form, as inferred from a pronounced streak in the scattering pattern, accompanied with Bragg spots stemming form the local ordering within the particle string. The oriented strings arise because of the viscoelastic nature of the suspending medium and have been observed previously for macroscopic and micrometer sized colloids (Michele et al., Rheol. Acta 16: 317 1977 and Scirocco R, Vermant J, Mewis J, JNNFM 117 (2-3): 183-192 (2004) - suspended in viscoelastic media.

Wednesday  6:10  Casco Bay Exhibit Hall

**Mason numbers for magnetorheology**

Daniel Klingenberg¹, John C. Ulicny², and Mark A. Golden³

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It is well known that experimental data for the apparent viscosity of an electrorheological fluid as a function of shear rate and field strength can often be represented as a single function of the Mason number, which represents the relative importance of hydrodynamic and field-induced forces. However, such a collapse is rarely obtained for magnetorheological (MR) fluids, mainly because of nonlinear magnetization. We define a new Mason number in which the magnitude of the magnetic field-induced forces is expressed using the suspension magnetization instead of the magnetic field strength. We show that experimental data for the viscosity of an MR fluid as a function of shear rate and magnetic field strength can be represented as a single function of this new Mason number. Implications of employing this new Mason number for experimental methods, modeling and simulations will be discussed.

Wednesday  6:10  Casco Bay Exhibit Hall

**Reciprocity relations between Stokes flows of viscous and viscoelastic fluids**

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Linear response theory of thermal fluctuations or driven motion of tracers in viscous and viscoelastic materials is the basis for many recent applications in microrheology. The emphasis for this lecture is on hydrodynamics and the associated deformation fields for incompressible viscoelastic materials, for various geometries and driving conditions. Exact solutions for Stokes flow of viscous fluids, without and with inertia, extend naturally to viscoelastic fluids by straightforward prescriptions, called reciprocity relations; these prescriptions apply for arbitrary sources and geometries. Two special Stokes singularities form the basis thus far of microrheology experiments and their interpretation: a prescribed velocity on a translating sphere and a stationary point source of force. We revisit and amplify these examples as an illustration of the reciprocity relations, focusing on measurable non-inertial and inertial features. Next, we illustrate the generality in source type and geometry of linear response theory by analyzing the linear response for a nonlocal, planar source of unsteady stress. Further applications are suggested.

Wednesday  6:10  Casco Bay Exhibit Hall

**Transient micro rheology of heterogeneous gels**

Jun Sato and Victor Breedveld

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Particle tracking micro rheology offers the opportunity to study the microscopic structure and mechanical properties of complex fluids. The use of colloidal tracer particles to probe the local rheology on micrometer length scales poses the challenge to match microscopic properties with bulk measurements in a rheometer, but also offers the opportunity to study microscopic phenomena that are inaccessible with a macroscopic rheometer. Many complex fluids, for example, exhibit heterogeneity on length scales that can be probed efficiently with colloidal tracers (0.1-10 micrometer). For such samples, the analysis of particle tracking data in terms of microstructure and micro rheology requires new approaches to quantify heterogeneity, especially in dynamically evolving systems. In this presentation, we will use salt-induced morphological changes in block copolymer hydrogels to illustrate the usefulness of transient micro rheology to quantify microstructural dynamics in complex fluids. In a dialysis cell for micro rheology that was developed by our group, aqueous block copolymer solutions were exposed to aqueous media with varying concentrations of NaCl. In previous work with a conventional macroscopic rheometer, it had been found that the addition of salt has a pronounced effect on macroscopic rheology. Here, micro rheological experiments will be presented with colloidal tracers ranging from 0.080 to 1.0 micrometer in diameter. Quantitative analysis of transient micro rheology and heterogeneity was performed with newly developed statistical analysis methods, which will be presented in detail. The use of different tracer sizes and the ability to manipulate the salt concentration in the dialysis cell have provided unique insight about structural evolution of the heterogeneous hydrogels in response to solvent composition changes. Images of the gel structure obtained in the dialysis cell with laser confocal microscopy supplement the microrheological data.
Wednesday 6:10 Casco Bay Exhibit Hall

**The characterization of droplet generation in branched microchannel**

Sung Sik Lee, Duwon Choi, Yoonjae Yim, Kyung Hyun Ahn, and Seung Jong Lee

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

The droplet generation in microchannel flow has been studied in the past decade. It is important to characterize the size and the input flow rate in order to manipulate the small volume (pico/nanoliter size) of droplets for chemical and biological application. We characterized the droplet generation using dimensionless expression. The droplets were generated with aqueous phase (glycerin and water) and oil phase (corn oil) in branched channel (T-junction and cross shape etc.). The two immiscible fluids made an interface at the junction of the inlet and main channel. The discontinuous fluid penetrated into the main channel and a droplet was generated. The sizes of the droplets were adjusted by changing the flow rate. When we plotted the dimensionless droplet length (l/d, l: droplet length, d: channel width) as a function of the dimensionless flow rate (the ratio of aqueous and oil phase flow rate), it showed power-law correlation. Using the scaling method, we could investigate the effects of viscosity ratio and elasticity on droplet generation size in T-junction geometry (every width and depth is 75µm). Increasing the viscosity ratio by adding glycerin to water, the power index n values are decreased (e.g. viscosity ratio = 0.02: n = -0.49, viscosity ratio = 0.22: n = -0.97). We expect this characterization method could facilitate tuning the design of the T-junction and choosing the flow rates resulting in sizes of the droplets required for specific applications.

Wednesday 6:10 Casco Bay Exhibit Hall

**Colloidal particle suspension flow and transport behavior in small channels by Magnetic Resonance Microscopy**

Jennifer R. Brown, Joseph D. Seymour, Sarah L. Codd, Giles R. Cokelet, and Magnus Nydén

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Colloidal suspensions cause complex and often non-Newtonian fluid flow behavior in many systems, from human blood flow in the microvascular system to flow in biomedical devices. Magnetic Resonance Microscopy (MRM) is ideal for studying opaque suspensions as it is non-invasive with the ability to measure spatially resolved and bulk diffusion and velocity. The research addresses both shear induced particle migration and aggregation of human blood in a Couette rheometer and model colloidal behavior when flowing in a small diameter capillary. The behavior of red blood cells (RBCs) under varying conditions of aggregation and interparticle forces are analyzed using RBCs in albumin-saline, in plasma and with added Dextran to enhance aggregation. Using the Quemada equation and MRM velocity images of blood exposed to a non-uniform shear rate in a small gap Couette, the first direct measurement of an inhomogeneous particle distribution across the gap with cell depletion at the walls was made. The model oil-filled hard sphere colloids are "MR-active" due to the ability of MRM to spectrally resolve the oil within the hard shell particle from the water in the suspending phase, allowing for the potential to track the dynamics of the two phases in a colloidal suspension independently. Experimental implementation is non trivial due to the relatively large amount of water in the suspending phase which limits the dynamic range of the receiver. A T1 inversion pulsed gradient spin echo method is applied to circumvent this difficulty. The propagator, the probability of spin displacement, for each phase can then be measured and the dynamics of the suspending fluid compared to the particle dynamics. Data for flow in a 1 mm capillary is presented. Two phase transport models depend on differences between the particle and fluid phase velocity and MRM can quantify this effect. The hope is that suspension dynamics and microstructure data obtained by MRM in these ideal systems can be applied to modeling in broader applications.

Wednesday 6:10 Casco Bay Exhibit Hall

**Biomechanics and micro-rheology in a primitive virtual cell**

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Recently, a computational model of cell biomechanics has been introduced, called the Sub-cellular Element Model. The model is primarily designed to represent deformable cells in multi-cellular systems, but can also be used to represent a single cell in more detail. Within the model framework, a cell is represented by a collection of elastic elements, interacting with one another via short-range potentials, and dynamically updated using over-damped Langevin dynamics. We are testing whether this model yields viscoelastic properties consistent with those measured in recent years from bead micro-rheometry techniques and particle tracking micro-rheology experiments on single living cells. Preliminary results on creep response curves from bead micro-rheometry are encouraging.

Wednesday 6:10 Casco Bay Exhibit Hall

**Effect of nanofluid on bubble behaviors and CO2 absorption**

Wun-gwi Kim, Hyun Uk Kang, and Sung Hyun Kim

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Nanofluid is a suspension containing nanoparticles of 1 to 100nm suspended in a conventional base fluid. Nanofluids have attracted great interest owing to their greatly enhanced thermal properties as well as potentialities for enhancing the mass transport property. This study examined the CO2 absorption and the bubble behaviors in the nanofluid. Experimental analysis was performed using the bubble type absorber. The concentration of nanoparticles and the rheological properties of the base fluid were considered as major parameters of bubble behaviors and the mass transfer performance of CO2 gas into the liquids. Rheological properties were varied by regulating the fraction of particle or addition
of PMMA. The results showed that the high viscous property made the initial outspread of gas bubble small and the high elastic property made bubbles move to the center of column. In the absorption experiment using the 5wt% nanofluid, the absorption rate of the first 1 minute increases 79% in water and 17% in 0.05M amine solution. The total absorption amount increases 0.16 L in water and 0.38 L in amine solution. Nanoparticles in nanofluid could crack the gas bubbles and increase the contact area between gas bubbles and liquid. Through the results of absorption performance, we suggested that nanoparticle could have surface renewal effect on gas-liquid interface, and nanofluid could intensify the reactivity between amine and CO2 component.

Wednesday 6:10 Casco Bay Exhibit Hall
Rheology and phase behavior of nanostructured polyurethane/POSS hybrid dispersions prepared from homogeneous solution polymerization
Samy A. Madbouly, Joshua U. Otaigbe, Ajaya K. Nanda, and Douglas A. Wicks
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Reinforced nanostructured polyurethane-POSS hybrid films were prepared with up to 10 wt % of functionalized polyhedral oligomeric silsesquioxanes (POSS) using homogenous solution polymerization or the so-called acetone process. This process can produce environmentally-friendly aqueous PU dispersion which can in situ polymerize in the presence of POSS to produce PU-nanocomposites with no organic solvent (the acetone will be evaporated at the end of the dispersion process). The effect of POSS on the rheological behavior of this important class of materials has been investigated over a wide range of temperature (-100 to 230 °C). POSS was found to react strongly with only the hard segments of PU (urethane segment), while the polyester soft segments were not affected by the presence of POSS. This experimental fact was confirmed by the increase in the Tg of the hard segments with increasing concentration of POSS as measured by DSC and dynamic rheology in the rectangular torsional mode configuration. The incorporation of POSS to the PU-hard segments was also found to have strong influence on the microphase separation temperature (TmPS) of the hard and soft segments, i.e.; the TmPS shifted by 30 °C to higher temperature at 10 wt% POSS. The viscoelastic material functions were found to be well described by the time-temperature-superposition principle at low temperature range, lower than the TMPS (130 °C); at higher temperature the principle is no longer valid. Furthermore, thermal characterization and wide angle X-ray diffraction (WAXD) did not reveal any gross phase heterogeneity due to the inclusion of POSS moieties.

Wednesday 6:10 Casco Bay Exhibit Hall
Rheology and crystallization behavior of nanostructured mPP/PC blend prepared via in situ polymerization and compatibilization
Samy A. Madbouly and Joshua U. Otaigbe
School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States

Reactive polymer blends with nanoscale morphologies as small as 50 nm have been prepared from in situ polymerization and compatibilization of macrocyclic carbonates with polypropylene modified with small amount of maleic anhydride-reactive groups (0.5 wt%) in a batch mixer. Crystallization and gelation behavior of mPP in the blends were investigated thermally (DSC) and rheologically. The DSC measurements revealed a considerable increase in the crystallization kinetics in the blends compared to that of the pure mPP. The high crystallization rate in the blends was attributed to the nanoscale morphologies produced during the in situ polymerization and compatibilization which can act as a nucleating agent for the crystallization process of mPP. The viscoelastic material functions of the blends, such as dynamic shear moduli, G' and G'', complex shear viscosity, η', and tanδ were measured isothermally at different temperatures near the crystallization (gelation) point of mPP over a wide range of frequency. The gel point, tgel, evaluated from the point of intersection in versus crystallization time obtained at different constant shear frequencies, where is no longer frequency dependent and all curves crossover indicating the validity of Winter-Chambon criterion. The onset of gelation point at constant temperature was substantially shifted to shorter time in the blends of up to 20 wt% PC in good agreement with the DSC measurements. The kinetics of the gelation process was also investigated in detail for this system rheologically.

Wednesday 6:10 Casco Bay Exhibit Hall
Evaluation of viscous behavior for immiscible polymer blends
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In the present study, the viscosity of two immiscible blends including polymethylmethacrylate and polystyrene as well as polydimethylsiloxane and polyisobutene have been measured. In contrast to previous works [Grizzuti, N., Buonocore, G., Iorio, G., J. Rheol., 44, 149-164 (2000)] and [Friedrich, C., Gleinser, W., Korat E., Maier, D., Weese, J., J. Rheol., 39, 1411-1425, (1995)], the present data have been obtained for a different range of compositions and shear rates. Several predictive and semi-emperical models have been compared with the experimental results. comparison between the experimental results and emulsions viscosity models allows one to modify them and also to give a contribution towards the understanding of the rheological behavior of immiscible polymer blends.
Block copolymers, termed compatibilizers, are often added to immiscible homopolymer blends to improve blending and control the morphology. In its traditional role of improving dispersion, compatibilizers can play two roles (1) reduce the interfacial tension, thus promoting drop breakup and (2) suppress coalescence. Here we will show that the property of coalescence suppression can be used to realize unusual morphologies in polymer blends.

We will demonstrate this in blends of poly(dimethylsiloxane) (PDMS) and poly(isobutylene) (PIB), compatibilized by a PIB/PDMS diblock copolymer. The compatibilizer is able to suppress coalescence only if PDMS is the continuous phase. If the samples are made in a single step, the minority phase always becomes the dispersed phase, for example, a blend with 20% PIB has a simple PIB-in-PDMS morphology. However, this can be changed by controlling the sequence of blending. For example, a compatibilized PDMS-in-PIB blend containing 60% PIB was blended with additional PDMS to achieve the same overall composition of 20% PIB. This blend, prepared in two steps, had an unusual PDMS-in-PB-in-PDMS morphology. Such morphologies are called "double emulsions" in the oil/water emulsion literature. Generally, the PDMS-in-PB-in-PDMS blends prepared by the two-step mixing process behaved rheologically like PIB-in-PDMS blends, but with a higher effective volume fraction of the drop phase.

This principle of controlling the phase continuity by varying the sequence of mixing is well-established in the small-molecule emulsion literature. We show that the same principle can be applied to immiscible polymer blends provided the compatibilizer can suppress coalescence.

We study experimentally the behavior of suspensions of noncolloidal particles in yield stress fluids. Our aim is to link the paste properties to the yield stress fluid properties as a function of the particle volume fraction independently of the physicochemical properties of the yield stress fluid and particles, i.e. we focus on the purely mechanical contribution of the particles to the paste behavior. We perform this study with various yield stress fluids (with different yield stress physical origins) and with particles of various sizes and with different surface properties. We find the universal laws linking the paste properties in the solid regime (elastic modulus, yield stress) to the suspending paste properties (independently of their physical origin) and to the particle volume fraction (independently of their size and surface properties). We show, in agreement with recent micromechanical results, that the elastic modulus/concentration relationship is linked to the yield stress/concentration relationship through a very simple law.

Linear viscoelasticity (oscillatory shear in the temperature range \( T_e < T < T_e + 90 \, \text{K} \)) and segmental dynamics (measured by dielectric spectrometer) are studied in polystyrene/poly(vinyl methyl ether) miscible polymer blends, where the low-\( T_e \) component PVME dominates the dielectric response. Such miscible blends with weak interactions and large \( T_e \) have concentration fluctuations that broaden the distribution of segmental relaxation times. This distribution narrows as temperature is raised, leading to the failure of time-temperature superposition for the terminal dynamics measured in oscillatory shear response and segmental dynamics observed in dielectric response. Using the tube model, we quantitatively compare dielectric and mechanical results. At low temperatures, the effective time scale for motion of a Kuhn segment is near the long-time end of the distribution of segmental relaxation times of PVME, in both the pure and blended states. The slowest relaxing segments thus dominate the longer-time relaxation processes of the chains.
simulation results which imply a direct correspondence between the microscopic model and the rheological properties of the system, via a group theoretical contribution method applied to the various interaction modes.

Wednesday  6:10  Casco Bay Exhibit Hall  PO34

Three-dimensional simulations in contractions: Diverging flow, off-centre velocity maxima and “cat's ears”
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Contractions flows of viscoelastic fluids are a classical benchmark problem in computational rheology. Although a concerted research effort in this area over the last twenty years or so, by several groups worldwide, has resulted in significant strides in our understanding of such flows, the numerical simulation of viscoelastic fluid flow in contractions is still remarkably challenging, with steady solutions achieved for frustratingly low levels of elasticity and with only limited numerical accuracy in most cases.

The current study focuses on the divergent flow regime that is frequently observed in contraction flows of highly elastic fluids. This "anomalous" phenomena is well known, being first observed by Cable and Boger [1], although not completely understood. It was long assumed that inertia was necessary for divergent flow to be observed in contractions, until very recently Alves and Poole [2] put forward a simple explanation, and demonstrated that it can also be observed under inertialless flow conditions.

In this work we investigate numerically the flow of a UCM fluid in a 3D planar smooth contraction, inspired by the recent experimental work of Poole et al [3]. These authors observed a remarkable 3D jet-like structure with large velocity overshoots close to the flat sidewalls. Given the similarities of the velocity profiles observed in the 'neutral' direction along the centreplane and the silhouette of a cat's head, Poole et al dubbed these profiles "cat's ears". Here we demonstrate that it is possible to reproduce this phenomenon, at least qualitatively, under creeping flow conditions and using a constant-viscosity viscoelastic model (UCM). Also, we show its relation to divergent flow, and consequently the importance of the extensional properties of the fluid.


Wednesday  6:10  Casco Bay Exhibit Hall  PO35

Prediction capability of a constitutive equation derived from reversible network with non-interacting dumbbell model
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In our previous work, we have performed Brownian Dynamic simulation to investigate the capability of reversible network with non-interacting dumbbell model proposed by Cifre et al. (J. Non-Newtonian Fluid Mech. 113 (2003) 73-96) to predict the shear and elongation properties of polymer solutions and melts. We have shown that, with the modification in connector force law and adjusting the association and dissociation functions, the model predicts properly the shear and elongation properties of both associative and non associative polymeric fluids. In the present work, we derived a constitutive equation from the model by superimposing the effects of velocity field and association/dissociation processes on the evolution of configuration tensor of the model molecules. The capability of the newly derived constitutive equation in predicting the rheological properties of polymeric fluids is investigated extensively. Furthermore, the predictions of the constitutive equation are compared to the predictions obtained from the Brownian Dynamics simulation to investigate the effect of approximations that used in the derivation of the constitutive equation.

Wednesday  6:10  Casco Bay Exhibit Hall  PO36

Cavitation between a moving sphere and a plane in near contact hydrodynamic flow
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Consider an experiment in which a sphere settles in a viscous fluid under gravity toward a flat plane for a certain period of time. After this period of time, the direction of gravity is reversed and the time to reach the initial starting position is measured. The creeping flow equations are reversible and would predict that the time to reach a particular point above the plane would equal the time that it settled towards the plane. Continuum predictions for a sphere released under gravity in a Newtonian liquid are not consistent with experimental observations when a particle comes close to contacting another particle or a containing wall. Under these circumstances, the continuum approximations break down. Irreversibilities are observed in thin-gap particle interactions. Continuum theory predicts negative pressure between a plane and a moving sphere, but negative pressure is patently impossible in the physical world. Hence, when the sphere is falling away from the plane, a bubble or cavity should appear in the close contact region. Depending on the size, the density, and the roughness of the sphere, the irreversibility may be caused by roughness, cavitation, or both. The results of these preliminary experiments show excellent agreement with our cavitation hypothesis.
Visualization of the distribution of glass fibers in molten polypropylene through a circular die
José Pérez-González, Emilio Vázquez-Otero, and Lourdes de Vargas
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A rheological characterization of polypropylene reinforced with short glass fibers under continuous extrusion through a circular die was performed in this work, along with a visualization of the distribution of fibers inside the die. The extrusion was performed at different temperatures above 210 °C in a single screw extruder. A borosilicate glass capillary was adapted to the extruder to perform the visualization of the distribution of fibers during flow. For this purpose a laser light sheet was sent through the capillary in a direction perpendicular to the flow. Photographs of the light scattered by the fibers were acquired with a CCD camera, and the patterns of the scattered light intensity were further analyzed to relate them with the average distribution of fibers inside the die for different flow conditions. The extrudates obtained for each flow condition were also analyzed by optical microscopy to register their morphology and to compare the fiber distribution in the solid state with that in the melt. Rotation and bending of the fibers were observed in the region near the die wall, as well as a strong orientation near the center. On the other hand, migration of fibers towards the capillary axis was enhanced when increasing the concentration of fibers, as well as at the onset of melt fracture.
Enthalpic viscosity
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The Carreau's equation, in its classical form, predicts an infinite (exponential) decrease of viscosity at infinite strain rate. Modification of the Carreau's equation includes a constant viscosity term. The validation of the existence of this viscosity term, which we call "Enthalpic Viscosity" versus "Entropic Viscosity" for the rest of the Carreau expression, is difficult to prove experimentally. Regression fits with or without the Enthalpic Viscosity term are equally good. We introduce a novel experimental procedure in a dynamic rheometer to prove, unequivocally, that such a viscosity term exists and has perhaps great significance in terms of long term entanglement stability.

Time-dependent relaxation in cellulose based gels
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Cellulose is a naturally-occurring organic polymer which has been used extensively as a thickener for industrial products such as paints and food materials. Understanding the time-dependent behavior of this polymer and its derivatives is therefore critical for the processing of materials containing them. We have studied the properties of concentrated solutions of low and high molecular weight hydroxyethyl cellulose (HEC) as well as hydrophobically modified HEC in the linear and non-linear regimes. We monitor the evolution of the structure of the materials by imposing a high strain for a fixed period of time, waiting a time tw, then apply a small (linear) strain and studying the response as a function of wait time. In this poster, we will present our results for the different materials and concentrations.

Rheology of blood in men and pre-menopausal women: Potential risk factors for development of cardiovascular diseases
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According to official statistical data, morbidity and mortality related to cardiovascular diseases and especially myocardial infarction are significantly lower in pre-menopausal women then in age-matched men. The nature of this phenomenon is not well understood. We hypothesized that the explanation could be that due to regular blood loss, rheological properties of pre-menopausal female blood are superior to those of male blood. The difference might be due to a lower hematocrit and a greater population of young and a smaller population of old red blood cells (RBCs) in female blood. We demonstrated that young RBCs have higher deformability than old ones. We revealed that male RBCs had significantly lower deformability compared to that in pre-menopausal female RBCs, which reduces RBC ability to enter the smallest capillaries. In addition, male blood was found to have a higher hematocrit and whole blood viscosity. Oxygen Delivery Index, calculated as a ratio of hematocrit to blood viscosity, was found to be significantly lower in male blood. Decreased oxygen delivery due to higher blood viscosity along with decreased RBC deformability may contribute to a higher risk for the development of cardiovascular diseases. We suggested that regular blood donation could reduce hematocrit and blood viscosity, improve RBC deformability, and enhance oxygen delivery to tissues in men by increasing the amount of young RBCs and decreasing the amount of old RBCs. Several epidemiological studies support our hypothesis regarding the advantage of blood donation. It was found that in a large group of middle-age men, the risk of heart attack was over 85 percent lower among blood donors. Another study showed that men, who had donated blood once a year, were at almost a twice lower risk in having a heart attack compared to those who had never donated blood. Collectively, these data provide strong evidence of the rheological benefits of regular blood loss/donation for reducing the risk of heart disease.

Gastric mucin exhibits pH Dependent sol-gel transition
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The viscoelastic and gel-forming properties of the gastric mucus layer are crucial to its ability to protect epithelial cells from damage by ingested substances and highly acidic gastric juice created in the stomach. Previous experiments have presented evidence that gastric mucin, the glycoprotein content of mucus responsible for its gel-forming properties, undergoes a sol-gel transition from solution at neutral pH to a soft viscoelastic gel below about pH 4. The bulk rheology data presented here on a model system of purified porcine gastric mucin (PGM) confirm this by showing that there is a qualitative change to a more solid-like response at low pH values. At pH 4, PGM is very nearly a critical gel by the criterion of Winter and Chambon that the frequency dependent viscoelastic moduli, G'(ω) and G''(ω) follow power-law scaling with approximately the same exponent n. These studies further explore the effects of pH on material properties such as yield stress and shear thinning behavior, as well as the influence of varying salt concentration and temperature in this system.
Determining motor inertia of a stress-controlled rheometer for more accurate measures near speaking frequencies
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Viscoelastic quantities over 50Hz are critical in the study of vocal fold-related tissues. Total inertia value and accuracy, however, limit the upper frequency of accurate data collection on a stress-controlled rheometer. Plate and sample inertia are calculated directly, but motor inertia must be determined experimentally. The present study compared two motor inertia-determining methods for a stress-controlled rheometer using Newtonian and non-Newtonian fluids. For Method 1 dynamic measurements of Newtonian Brookfield PDMS, viscosities 975cP and 11880cP, were collected using a 40mm parallel plate on the Bohlin CVO120 stress-controlled rheometer. Phase was analyzed at 5-70Hz and for motor inertia values of 50-150% of the manufacturer's value. Phase of the 975cP fluid satisfied the 89-90 deg. Newtonian criterion for inertia values 90-110% of the manufacturer's value at 5Hz and for an inertia value 100% of the manufacturer's value at 12Hz. Phase of the 11880cP fluid satisfied the Newtonian criterion for inertia values 50-110% of the manufacturer's value at 5Hz. For Method 2 dynamic measurements of non-Newtonian NIST SRM-2490 were collected using 10mm and 60mm parallel plates. Properties of the fluid generated a different resonant frequency (i.e., frequency at which shear strain per Nm torque reached a maximum) for each plate when G''/G'<1. Using a linear equation of motion with inertia, viscosity, and elasticity coefficients, G' expressions for both plates were equated and motor inertia was solved for algebraically. Motor inertia values reached a plateau and variability was a minimum, 2-3%, at three frequencies lying midway between the two resonant frequencies. Motor inertia values in the plateau corresponded to values using Method 1 and the 975cP Brookfield fluid, but with less variability. In conclusion, Method 2 using NIST SRM-2490 is a reasonable alternative to Method 1 and provides explicit derivation and error analysis to confirm accuracy of result. Work supported by NIH-NIDCD (F31 DC 008047-01).

Using rheological and tribological methods to better assess mouthfeel of food systems
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Many rheological models available in the food industry do not fully explain differences in the perception of texture of food systems. Nowadays, in order to assess texture of a final product, manufacturers turn to sensory panels, which are time consuming, expensive, and susceptible to a large range of variations. Developing instrumental methods to score food texture would greatly benefit the food industry to developing more consumer acceptable food products. We used a tribological device developed by Anton Paar to measure differences in texture perception not detected by bulk rheology. We scored the sensory properties of chocolate samples with varying particle size distributions and melting profiles, hydrocolloid solutions, starch dispersions with varying degrees of sliminess, and commercial dairy emulsions with varying fat contents. The tribological and rheological properties of chocolate were compared to sensory scores, which tested for creamy mouthfeel. Higher melting profile and particle size distribution evoked a significant reduction in the friction coefficient of the samples as a function of sliding speed. The impact of thermal transitions of the chocolate sample, and particle size distribution were directly correlated to frictional properties of the samples tested. Hydrocolloid solutions, starch dispersions, and dairy emulsions were tested for flow behavior and lubrication properties. These values were compared to sensory scores, which were rated for creamy mouthfeel, mouth coating, and thickness. From the Stribeck curves we were able to deduce that the choice of hydrocolloid played a far more important role in the tribological regime than fat content of the sample. The degree of sliminess correlated very well to the friction coefficient measured using the tribology device.

Gastropod locomotion: How tuned are the properties of the mucus?
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Common gastropods such as snails crawl on a solid substrate by propagating muscular waves of contraction on a viscoelastic mucus. Producing the mucus accounts for the largest component in the gastropod's energy budget, more than twenty times the amount of work used for crawling. Using a simple mechanical model, we show that the rheological properties of the mucus (shear-thinning) favor a decrease in the amount of mucus necessary for crawling, thereby decreasing the overall energetic cost of locomotion.
Rheological properties of lysozyme in ethanol-water mixtures

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We investigate the development of the rheological properties of lysozyme in ethanol-water mixtures as a function of the ethanol content. At a fixed lysozyme concentration, the variation of the ethanol concentration leads to the formation of a stress-bearing gel whose elastic modulus increases as the ethanol content increases. A preliminary interpretation suggests that conformational changes induced by the changing solvent conditions lead to localized interactions and, eventually, the formation of the elastic gel. We thus explore the possibility to use these systems as model systems for the study of gelation as function of interacting sites per molecule.

Viscoelastic characterization for optimization of the soft-tissue seal around osseointegrated lower-limb prosthetics

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The formation and maintenance of a soft-tissue seal is essential to the success of osseointegrated prosthetics used in the treatment of lower-limb amputees. Despite advances in percutaneous devices there still exist limitations which are exacerbated by the loss of the soft-tissue seal. The chief failure modality of these devices is epidermal regression. Regression is the product of disruptions of the mechanical behavior of the tissue due to changes in its mechanical integrity. To avoid regression, it is necessary to develop an accurate way to describe and then minimize the contribution of stress concentrations to tissue degradation. With this in mind we conducted rheometer experiments at 37°C on 6mm dia. whole human skin samples at 1 and 10% strain. The rheometer provided the elastic and viscous moduli for clinically relevant frequencies between 0.5 Hz and 20 Hz. Using this data, with stress-relaxation results, a novel viscoelastic model for inclusion in an ABAQUS based finite element model (FEM) of the interface region was developed. The model includes an analytically rigid abutment and a deformable monolayer. The abutment is displaced to simulate levels of activity, producing the quasi-static, maximum displacement of the interface region. The rheometer provided elastic moduli ranging from ~3000 Pa at high frequencies to ~100 Pa at low frequencies and viscous moduli ranging from ~360 Pa at high frequencies to ~30 Pa at low frequencies. More advanced FEMs will be needed for the optimization of the prosthetic system but preliminary results demonstrate the utility of a mechanics based approach in describing the stresses of the interface region. Future rheometer experiments will create a more detailed picture of the mechanical behavior of human skin by examining the epidermis and dermis individually as well as the affect of titanium nano-particles on the mechanical behavior of skin. Ultimately, the goal is to design a stress-reducing cuff as a supplemental component for the osseointegrated prosthetic system.

Time dependent effect of D-penicillamine on the viscosity of hyaluronic acid solutions

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The polyelectrolyte hyaluronic acid (HA, hyaluronan) is an important component in synovial fluid. Its presence results in highly viscoelastic solutions with excellent lubricating and shock-absorbing properties. In comparison to healthy synovial fluid, diseased fluid has a reduced viscosity. In osteoarthritis, this reduction in viscosity results from a decline in both the molecular weight and concentration of hyaluronic acid HA. D-Penicillamine affects the rheology of bovine synovial fluid, a model synovial fluid solution, and its components, including HA. In order to understand how D-penicillamine modifies the viscosity of these solutions, the rheological properties of sodium hyaluronate (NaHA) in phosphate-buffered saline (PBS) with D-penicillamine were studied as function of time, D-penicillamine concentration (0 - 0.01 M), and storage conditions. Penicillamine has a complex, time dependent effect on the viscosity of NaHA solutions; it reduces the zero shear rate viscosity of a 3 mg/mL NaHA in PBS by ca. 40% after 44 days.

Slip during viscometric flows of viscoplastic liquids

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We tested a modified Couette fixture for a strain-controlled rotational rheometer with vertical grooves both on the bob and on the cup. The grooved fixture reproduces the viscosity of a few Newtonian mineral oils with negligible deviation for a wide range of shear rate, which indicates that the presence of the grooves does not affect significantly the flow kinematics. We obtained flow curves with the standard smooth Couette geometry, with the vane, and with the grooved geometry. In the high shear rate range, the curves for all geometries are nearly coincident, suggesting that no wall slip occurs in this range. However, for lower shear rates the repeatability is unacceptably poor for both the standard Couette and the vane geometries. Moreover, all curves obtained with these two geometries present a discontinuous slope at the shear rate value above which the data becomes repeatable. The flow curves obtained with the grooved Couette geometry, however, present no slope discontinuity, and the repeatability is excellent. We also perform flow visualizations of the flow due to gravity of a column of the same carbopol solutions in vertical tubes of different diameters. The inner wall of some of these tubes have also grooves. There is a threshold diameter below which there is no flow. For the grooved tubes, this limiting diameter corresponds to a wall shear stress slightly above the yield stress measured.
with the grooved Couette geometry, as predicted theoretically. For the smooth tubes, the threshold diameter is much smaller, indicating wall slip. Terminal velocity curves as a function of the wall stress are given, both for smooth and grooved tubes.

Wednesday 6:10 Casco Bay Exhibit Hall

**Correlation length of salt-free polyelectrolyte solutions investigated by rheology and SAXS**

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Effects of polyelectrolyte charge density, counterion type, solvent dielectric constant and solvent quality on the semidilute correlation length $\xi$ were studied at 25°C for solutions in ethylene glycol (EG), distilled water (DW) and N-methyl formamide (NMF). Charge density effects in partially quaternized poly(2-vinyl pyridine) with chloride counterions in the good solvent EG covering quarterization extents from $\alpha = 0.03$ to 0.55 were studied with results in agreement with the de Gennes scaling model. Solvent effects on the correlation length of strongly charged polyelectrolytes with $\alpha = 0.6$ were investigated using rheology and SAXS. The correlation length of polyelectrolytes in solution greatly depends on the solvent dielectric constant and solvent quality. The concentration dependence of the correlation length obtained from rheology agrees with the de Gennes scaling prediction $\xi \sim c^{-1/2}$, with larger correlation length in solvents of lower dielectric constant owing to a lower effective charge on the polyanion. The de Gennes scaling was also observed in SAXS for the polymer with chloride counterions in EG (good solvent). In contrast, a weaker concentration dependence was found for SAXS results with iodide counterions in NMF, EG and DW. A clear transition of the charge on the polyion. The de Gennes scaling was also observed in SAXS for the polymer with chloride counterions in EG (good solvent). In contrast, a weaker concentration dependence was found for SAXS results with iodide counterions in NMF, EG and DW. A clear transition is related to the chain collapse due to counterion-induced attractions between the strongly dipolar condensed iodide-(quaternized ammonium) ion pairs on different monomers, effectively making EG a poor solvent for the polyion with iodide counterions. This is the first evidence in the literature that the counterion can change the effective solvent quality of a given polyelectrolyte/solvent pair. Counterion size, solvent dielectric constant, and charge density impact the counterion-induced attraction of polyelectrolytes in solution.

Wednesday 6:10 Casco Bay Exhibit Hall

**Synthesis and rheology of hydrophobically modified poly(vinyl alcohol)[HMPVA] using gallic acid derivatives**

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Hydrophobically modified [HM] polymers are used as viscosity modifiers/thickeners in the wide variety of industrial applications. Amongst the many polymers, poly(vinyl alcohol) [PVA] has showed great potential for hydrophobic modifications because of the presence of highly reactive -OH groups. In the present study, the hydrophobic modification of PVA was performed using a gallic acid derivative namely, methyl gallate with three hydrophobic side chains of -C8H17 alkyl groups. The hydrophobic compound, methyl gallate was coupled to PVA through the transesterification reaction. Furthermore, the altered solubility of the HMPVA was regained and enhanced by the subsequent reaction of HMPVA with 1,3-propane sultone, which incorporates the ionic charges on the polymer chain. HMPVAs with three different contents of methyl gallate were prepared and the structural characterization was performed by 1H and 13C NMR spectroscopy. The aqueous solutions of HMPVAs exhibited several fold enhancement in the viscosity as compared to their unmodified precursors at the same concentrations. The influence of polymer concentration and the hydrophobic content on the zero shear viscosity has been studied and explained using scaling laws. The dramatic increase in the viscosity of HMPVAs has been attributed to the formation of transient network as a result of the hydrophobic associations in the polymer chains. The aqueous solutions of HMPVAs at moderate concentrations, showed Newtonian behaviour at very low shear rates, shear thickening at intermediate shear rates and shear thinning at high shear rates. Furthermore, some HMPVA solutions showed flow instability at high shear rates.

Wednesday 6:10 Casco Bay Exhibit Hall

**Torque and normal force responses of glassy polymers: Evidence of the influence of side group beta-relaxations**

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Results from torsional stress relaxation experiments in which we measure the torque and normal force responses of two glassy poly(alkyl methacrylate)s, a polycarbonate (PC) and a polysulfone (PSF) are presented. Tests were performed at temperatures ranging from the dynamic glass transition (alpha-relaxation) to the first sub-glass transition relaxation (beta-relaxation) and in the sub-yield range of deformations (strains ranging from 0.02 to 0.045). We found a significant difference between the relaxation behavior of the normal force response and the torque responses for the two n-alkyl methacrylates, while the PC and the PSF showed similar relaxations for these two. We are able to attribute the behavior to the strong beta relaxations in the acrylates, i.e., the PC and PSF have weak beta relaxations and correspondingly weak normal forces. Also, following the scaling law relations of Penn and Kearsley, the derivatives of the strain energy density function with respect to the first and second invariants of the strain tensor were determined. The results are discussed in terms of such a representation as well as in terms of deviations from so-called neo-Hookean behavior.
Examination of the pom-pom constitutive equation for two polymers melts set

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To study of nonlinear viscoelastic properties of polymer melts many constitutive equations has been developed so far. Among them, the pom-pom model is suitable and useful to analyze of rheological behavior. The pom-pom constitutive model was introduced by McLish and Larson [1] for long-chain branch polymers. This model is based on the tube theory and a simplified topology of branched molecules. The primary constitutive model was modified by introducing local branch-point displacement [2], and the modified extended pom-pom model tried to overcome the previous shortages [3]. However, in order to complete the model evolution, it is necessary to examine the ability of the model to predict the rheological behavior of melts with a different sort of topology. For this purpose, two different domestic commercial data are examined in shear and extensional flows for polymer melts LDPE and HDPE. In general, the results from comparison between experimental data and the model predictions has been shown that the extended pom-pom model is capable to predict good the rheological behavior over range experimental data obtained by conventional experiments.


MD simulation of polymer melt: Chain architecture, potential model and DPD thermostat

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We studied the static and dynamic properties of polymer melt with different chain architectures (linear, star, ring) using molecular dynamics (MD) simulation. Polymer chains are modeled as beads connected by FENE springs. Two types of beads are used for the construction of a polymer chain, namely the soft beads (beads that interact with the soft DPD potential) and the hard beads (beads that interact with strong repulsive potential, e.g. the Lennard-Jones potential). In the soft beads system, polymer chains can easily cross each other, while in the hard beads system, chain crossing is strictly avoided, and therefore by comparing the simulation results directly, we can appreciate the effect of chain uncrossibility constraint on polymer dynamics. We also exploited the possibility (or the consequence) of using DPD thermostat in MD simulation of hard beads systems. The main reason we chose to use DPD thermostat is that to study the screening effect of hydrodynamics interaction in polymer melt, we need a thermostat scheme which preserves the hydrodynamic feature of the system. The DPD thermostat, satisfies the local momentum conservation condition, and is considered to be ideal for the studying of hydrodynamic problems. In this study, we mainly studied polymer melts with relatively short chains, and thus all simulation results on polymer dynamics are compared with the classical Rouse model.

Rheological modeling of warpage in polymeric products by plug-assisted vacuum thermoforming

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Thermoforming process is one of the most popular techniques in polymer processing due to its interesting capabilities. The fundamental defect inherent to the thermoforming technology is warpage of the products during their application which becomes particularly apparent under high temperatures. The warpage is understood as the process of non-uniform (heterogeneous) change of the geometrical dimensions of products in time resulting in a change (distortion) of their original form. In this work with rheological modeling of warpage specify the causes of this defect and the conditions for its development. Thereby, it is possible to work out in providing valid recommendations for partial and, in some cases, complete elimination of the defect.

Rheological method for prediction of the quality of dispersion in composites

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A method to predict the quality of dispersion of additives such as Talc, Calcium Carbonate in a polymeric matrix (Homo PP) by rheological experiments (MFI, RMS). The method allows to compare the extent of exfoliation of additives on a routine polymer. In fact, in this paper is discussed melt rheology as a method to characterize polymer-additives composites. This paper demonstrates the importance of how the additives were melt processed into the thermoplastic. Talc and Calcium Carbonate were added to Homo PP using extruder with a variation of screw speed (500 and 900rpm) and feeding rate (7 and 18 kg/hr). The degree of dispersion is interpreted in terms of the mean residence time in the extruder and shear intensity.
microscopy. We present data on a wide variety of polyolefins and ethylene copolymers. Examples from both tubular and continuously stirred reactors (CSTR) are included and compared. The distribution of both co-monomer and LCB were found to be dependent on the type of synthesis. End-use properties of these resins can reflect these differences in distribution of LCB and co-monomer even when the average co-monomer content and degree of LCB is similar. The distribution of the co-monomer as a function of molecular weight was determined using high temperature size exclusion chromatography coupled with an FTIR detector.

Wednesday 6:10 Casco Bay Exhibit Hall

Determination and analysis of the pressure dependence of the viscosity of molten polymers

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Viscosity measurements under elevated pressure were performed on PMMA, PaMSAN and LDPE melts, using a capillary rheometer extended with a pressure chamber. From the results it is clear that PMMA and PaMSAN have a very similar pressure dependence. The LDPE, which consists of very flexible chains, is much less sensitive to pressure. It was demonstrated that the data can be analyzed in terms of constant shear rate and constant shear stress pressure coefficients, each of which can be calculated by the direct method or by superposition of the viscosity curves. The constant shear stress pressure coefficients have the important feature of being shear stress independent for the three polymers under investigation. The constant shear rate pressure coefficients on the other hand turn out to depend on shear rate. The former should thus preferably be used in process simulations and modeling.

Wednesday 6:10 Casco Bay Exhibit Hall

Microstructure and LCB differences in tubular and CSTR polyolefins and ethylene copolymers

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The characterization of long chain branches (LCB) in polyolefins and ethylene copolymers is a long-standing issue. Even very small amounts of long chain branching can have a large impact on processing and melt flow. Recent advances in on-line chromatography detectors including multi-angle light scattering, viscometry and FTIR have greatly advanced the opportunity to characterize the distribution of these branches. Recent theoretical work, as well as experimental work on model branched polymers has indicated that the placement as well as the length of these branches is critically important to predicting their impact on rheological properties. Short-chain branches have far less impact on flow properties, but strongly influence the crystallinity of the polyolefins. For ethylene copolymers, the characterization is further complicated by co-monomers. We present data on a wide variety of polyolefins and ethylene copolymers. Examples from both tubular and continuously-stirred tank reactors (CSTR) are included and compared. The distribution of both co-monomer and LCB were found to be dependent on the type of synthesis. End-use properties of these resins can reflect these differences in distribution of LCB and co-monomer even when the average co-monomer content and degree of LCB is similar. The distribution of the co-monomer as a function of molecular weight was determined using high temperature size exclusion chromatography coupled with an FTIR detector.

Wednesday 6:10 Casco Bay Exhibit Hall

Viscous and elastic properties of linear and short-chain branched polyethylenes

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Linear and short-chain branched polyethylenes with a very wide range of molar masses, molar mass distributions and comonomer contents were characterized in shear. The linear and short chain branched PEs follow a relation between the weight-average molar mass $M_w$ and the zero shear-rate viscosity $\eta_0$ with a double logarithmic slope of 3.6 (and 1 for $M_w$<$M_c$) independently of the molar mass distribution and the kind and content of the comonomer.

The elastic recovery compliance $J^{\infty}_0$ of the LLDPEs increases with increasing molar mass $M_w$ - a result being surprising as this quantity was found to be constant for monodisperse samples (PS, PB, hPBd).

The resulting viscosity functions (by oscillatory measurements in the linear viscoelastic regime) were described with a Carreau-Yasuda-equation. The characteristic relaxation time $\lambda$ being a fitting parameter of that equation was found to be equivalent to the reciprocal crossover frequency $1/\omega_c$. $\lambda$ correlates with $M_w$ in the way $\lambda\sim M_w^{3.6}$ but is dependent on the molar mass distribution and the comonomer content. A broader molar mass distribution increases $\lambda$ while the addition of comonomers lowers this quantity. The width of the transition between the terminal and the shear thinning regime was found to increase with increasing molar mass $M_w$. It was also found that there is a linear correlation between this transition and the elastic recovery compliance $J^{\infty}_0$. The activation energy of the short chain branched PEs was found to increase linearly with increasing weight content of the side chains.
Elastic breakup of entangled polymers in shear: What is chain disentanglement?
Shi-Qing Wang, Pouyan E. Boukany, and Sham Sundar Ravindranath
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Chain entanglement and disentanglement are among the most important concepts in polymer science. They have been explored for six decades since the 1946 transient network theory of Green and Tobolsky. A quantitative description of chain entanglement arrived in the form of the reptation idea in 1971. Another 35 years have passed before we have reached the present moment when it is possible to visualize chain entanglement [1] in 2004 and contemplate a molecular mechanism for chain disentanglement in 2006 [2]. This work describes how our experiments [3] led to the development of a different approach in the study of polymer flow. The instrument setup involving simultaneous particle tracking velocimetric observations and conventional rheometric measurements, experimental results and new theoretical understanding are all presented to illustrate the direction our lab is taking in the future.


New understanding on polymer wall slip
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After intensive studies on the subject of polymer wall slip in the past fifteen years, it was our judgment that the subject is relatively well understood. However, a recently discovered molecular mechanism for chain disentanglement in polymer flow [1] prompted us to re-examine our understanding of polymer slip, in particular, the physics governing slip behavior of entangled polymers. We are able to predict, explain and show through experiment the behavior of "premature" slip, i.e., display of wall slip by entangled polymer melts, not during shear but only upon cessation of flow. This behavior has been reported once before as "delayed slip" [2], but caught no attention and never received any explanation as to why it occurred.


Distinguishing between shear banding and shear thinning behavior in entangled systems
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We attempt to distinguish between shear thinning and shear banding behavior for entangled micellar and polymer systems by measuring the velocity profile in various flow geometries. In flow geometries with significant inherent stress gradient, strongly shear thinning systems show velocity behavior that resembles that of shear banding. However, it is demonstrated that the difference between shear banding and shear thinning becomes clear in a narrow gap cone and plate geometry where the inherent stress gradient is negligible.

Cooperative networks: Viscoelastic control in solutions of wormlike micelles and polymers
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Mixtures of polymers and surfactants in solution are important in a wide range of applications including detergents, personal care products and oil recovery fluids impacting the chemical, pharmaceutical and petroleum industries. The objective of this project is creating synergy between the polymers and wormlike micelles allowing the properties of the solution, especially the rheology, to be tuned. Experimental protocols for studying the polymer-micelle mixtures include flow and oscillatory rheology, rheo-optics and phase mapping. Using theoretical models from surfactant and polymer science, this characterization provides tremendous insight into important length and time scales of the co-entangled network. Exploitation of solution conditions to increase the overall length of the wormlike micelles creates either entangled or branched networks, which changes the viscosity of the solution. Varying the solution conditions can change the rheology from Newtonian to shear thinning to shear thickening. The system of interest uses the widely studied combination of a cationic surfactant, cetyltrimethylammonium bromide, and hydrotropic salt, sodium salicylate, to produce viscoelastic solutions of wormlike micelles under a wide range of solution conditions. The polymer, hydroxyethyl cellulose, is added to the wormlike micellar solutions at several concentrations. The zero shear viscosity increases or decreases depending on the salt concentrations providing information on the cooperativity of the polymer-wormlike micelle networks. Overall, experimental control of pressure, temperature, macromolecule concentration and other variables allows structure-property relations of wormlike micelle-polymer cooperative networks to be measured.
Sensitivity and stability analysis of fiber spinning process accompanied by flow-induced crystallization

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Sensitivity of a viscoelastic melt spinning process accompanied by flow-induced crystallization (FIC) has been investigated by solving the linearized perturbation equations in the frequency domain. Also, results by frequency response method have been compared with dynamic transient solutions imposed with any sinusoidal disturbance. Resonant peaks of the final filament thickness with respect to tiny disturbances, which are frequently encountered in hyperbolic system, have been observed in the frequency region. It has been found that the sensitivity of the spinning system with FIC kinetics critically depends on the degree of crystallinity onto the spinline. In the case that the crystallinity of a filament is not reached to its maximum onto the spinline, the spinline tension increased by the FIC makes the system less sensitive to any disturbance, thus enhancing the process stability. However, the maximum crystallinity onto the spinline makes the system more sensitive due to the decrease of the spinline distance to be deformed.

Electromechanical response of highly filled SEBS/carbon conductive composites

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Viscoelastic and electrical properties of carbon filled elastomeric composites have strong dependence on factors such as filler concentration, morphology, dispersion degree and distribution (i.e. Payne effect). This fact makes interesting the study of the relation between those properties in this kind of materials. The present work pursues such goal trough the evaluation of the electrical behavior of conductive composites SEBS/carbon black/graphite during the application of a mechanical deformation process. Specifically, two types of deformation tests were performed at the time the electrical resistance was measured in situ: 1) static stress - strain and 2) creep - recovery, both carried out in flexural mode. In the first case, the electrical resistance of the composites showed a linear increment as stress and strain are increased, even when stages of mechanical behavior like yield and plastic regions were reached. In the second case, creep-recovery experiment, the electrical resistance presents little dependence on time when a constant load inside the linear viscoelastic region is employed; on the contrary, using a constant load beyond such region, resistance behaves in an analogous way to that of the mechanical response, it means, an instantaneous and a transient response as well as a recovery stage is exhibited.

Analysis of the upstream plane Poiseuille flow of a shear banding micellar solution and its relation with flow instabilities

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The upstream plane Poiseuille flow of a shear banding semidilute aqueous solution of 100 mMol/l cetylpyridinium chloride and 60 mMol/l sodium salicylate was studied in this work by particle image velocimetry (PIV). The experiments were conducted at 27.5 °C in a plane Poiseuille cell under controlled pressure conditions. A wide shear stress range covering the whole non monotonic flow curve typical of this sort of solutions was analyzed. The velocity maps upstream of the contraction were determined for the different flow regimes including stable and unstable flow conditions. At low shear stresses under stable flow conditions the velocity profiles upstream of the contraction appeared symmetric and showed the development of vortices. Once the critical stress for the onset of instabilities was reached, there was a spurt with a jump in shear rate of the order of 100 s⁻¹, which was followed by a pulsed flow and vertical oscillations of the vortices. Such oscillation of the vortices made the flow unstable in the high shear branch, in a way resembling the melt fracture regime during the extrusion of polymer melts, which suggests that this behavior is ubiquitous of highly viscoelastic fluids.

Effect of strain % on the viscosity-frequency curve of polymeric melt

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Routine frequency sweeps done in a dynamic rheometer are conducted at low % strain, usually 2-5%. Most of the published work on the influence of strain is done either in Stress Relaxation experiments, or at very large strain (LAOS), low frequency. We use a traditional dynamic rheometer and explore the range of % strain between 2% and 60%, for frequency sweeps in the range of 0.1-40 Hz. We fit the data with either a modified Carreau, or with the new formulation of Viscosity-w' introduced in another paper of this conference. We explore several resins, PMMA, PC, PP and EVOH. We analyze the influence of % strain not only on the Newtonian viscosity, but also on pseudo-plasticity of the melt, and on the Normal Forces. We conclude that % strain, even in this low range, plays an important role in the rheological response, and find a transitional behavior which varies with molecular weight as well as the type of resin.
Combining Small Angle Neutron Scattering (SANS) with a deformation field to probe structures under flow has led to significant advances in our understanding of complex fluids. We present here the design and operation of two new devices being developed for user experiments at the National Institute for Standards and Technology’s Center for Neutron Research. The first is a modified rheometer which allows simultaneously rheological and structural measurements. The apparatus uses the standard Couette geometry which allows structural information in the flow-vorticity (1-3) and shear gradient-vorticity planes where the incident beam is parallel to the shear gradient and to the flow direction respectively. This device enables a wide variety of measurements such as stress/strain flow curves and oscillatory deformations over a wide range of temperature (-20 to 150 °C). We give a brief report of recent experiments performed on a dispersion of acicular nanoparticles [1] and wormlike micelles [2]. Although use of the Couette geometry to probe structural changes under shear flow had remarkable success, the most important changes in fluid microstructure occur in the 1-2 plane and can not be accessed in this way. We have developed a new prototype Couette shear cell which allow measurements in the 1-2 plane with the additional ability of resolving position within the gap separation as the incident beam is parallel to the vorticity direction. The possibility to access spatial resolution in the gap is essential and critical for resolving shear-induced phase separation as the other 2 configurations available with the standard Couette cell (radial and tangential) probe the average structure through the gap. The prototype cell has already been successfully used in the case of wormlike micelle [3] and cubic phases under flow [4].


Active laser tweezer microrheology of colloidal suspensions
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Microrheology has recently emerged as a powerful experimental technique to study complex fluids. Measurements are performed by tracking the motion of small probe particles which are driven passively by thermal motion or actively with an externally applied force. One of the unique features of microrheology is the ability to characterize small sample volumes at micron length scales, making microrheology well suited for the study of biological materials. Colloidal suspensions serve as an ideal system for verification experiments because their linear and non-linear rheological properties are well understood. In this work, we present an active, oscillatory approach to laser tweezer microrheology. Micron sized polystyrene particles are trapped in a suspension of fluorinated ethylene propylene (FEP) with laser tweezers and oscillated at frequencies between 5 Hz and 90 Hz. The response of the particles is tracked with a quadrant photodiode and used to calculate the viscosity and viscoelastic moduli of the surrounding fluid. Measured viscosities for several solutions showed quantitative agreement with previously performed bulk and microrheological measurements [1]. Notable frequency thinning is observed at volume fractions greater than 0.30. The results are found to be in good agreement with recent theory [2].


Quantification of the effects of cellular microstructure on high density flexible foam mechanical properties
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Flexible foam materials are found in many modern day systems. The mechanical properties of foams, critical parameters specified by the function of application of the foam in a system, are directly linked to the structural and morphological features of the cellular structure of the foam. Cell size, size distribution, anisotropy orientation and strut parameters interact in complex ways to influence the overall physical behavior in which we are ultimately interested. These cellular parameters depend primarily on the density of the cellular material and the interaction of this with the space-filling nature of the cells. Prior important work relates foam mechanical properties to foam relative density: \[ \rho_{\text{relative}} = \frac{\rho_{\text{foam}}}{\rho_{\text{polymer}}} \]. However, these theories only correspond to the lowest 10% of the total range of foam relative densities thus leaving the other 90% of the range unstudied. This poster outlines the research steps we are undertaking in order to develop a complete understanding of foams over the full range of relative densities.
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**Plenary Lectures**

8:30 AM Vermont

**Monday, October 9**  
*Rheology of biopolymer networks*  
Paul Janmey  
*Departments of Physiology, Physics and Bioengineering, University of Pennsylvania*

**Tuesday, October 10**  
*Bingham Lecture*  
*Rheology and energy*  
Robert C. Armstrong  
*Department of Chemical Engineering, Massachusetts Institute of Technology*

**Wednesday, October 11**  
*Do you speak thermodynamics?*  
Hans Christian Öttinger  
*Department of Materials, ETH Zürich*

**Social Program**

**Sunday, October 8**  
**Welcoming Reception**  
7:00 PM – 9:00 PM Vermont/Connecticut/Rhode Island  
*Sponsored by a generous contribution from TA Instruments*

**Monday, October 9**  
**Society Luncheon**  
11:50 AM – 1:50 PM Casco Bay Exhibit Hall  
**Society Reception**  
7:00 PM – 9:00 PM Portland Museum of Art  
*Sponsored in part by a generous contribution from Malvern Instruments*

**Tuesday, October 10**  
**Society Business Meeting**  
6:10 PM Massachusetts  
**Awards Reception**  
7:00 PM Casco Bay Exhibit Hall  
*Sponsored by a generous contribution from Xpansion Instruments*  
**Awards Banquet**  
8:00 PM Vermont

**Wednesday, October 11**  
**Poster Session Reception**  
6:10 PM – 8:10 PM Casco Bay Exhibit Hall  
*Sponsored by a generous contribution from Anton-Paar USA*

The Society gratefully acknowledges the support by the Department of Chemical and Biological Engineering at the University of Maine in hosting the meeting. The Society also gratefully acknowledges the generous contributions of the event sponsors.