THE SOCIETY OF RHEOLOGY

74TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Radisson Hotel Metrodome
Minneapolis, Minnesota
October 13 - 17, 2002

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Meeting Schedule

Monday, October 14, 2002

8:30	E. S. Shaqfeh (PL1)			
9:20	Coffee			
9:45	MR1	FM1	AS1	CF1
10:10	MR2	FM2	AS2	CF2
10:35	MR3	FM3	AS3	CF3
11:00	MR4	FM4	AS4	CF4
11:25	MR5	FM5	AS5	CF5
11:50	Lunch			
1:30	MR6	FM6	AS6	CF6
1:55	MR7	FM7	AS7	CF7
2:20	MR8	FM8	AS8	CF8
2:45	MR9	FM9	AS9	CF9
3:10	Coffee			
3:35	MR10	FM10	SL1	CF10
4:00	MR11	FM11	SL2	CF11
4:25	MR12	FM12	SL3	CF12
4:50	MR13	FM13	SL4	CF13
5:15	MR14	FM14	SL5	CF14
5:40	End			
7:00	Society Reception			

Tuesday, October 15, 2002

8:30	R. G. Larson (PL2)			
9:20	Coffee			
9:45	MR15	FM15	SL6	GL1
10:10	MR16	FM16	SL7	GL2
10:35	MR17	FM17	SL8	GL3
11:00	MR18	FM18	SL9	GL4
11:25	MR19	FM19	SL10	GL5
11:50	Lunch			
1:30	MR20	FM20	HS1	GL6
1:55	MR21	FM21	HS2	GL7
2:20	MR22	FM22	HS3	GL8
2:45	MR23	FM23	HS4	GL9
3:10	Coffee			
3:35	SD1	CE1	HS5	GL10
4:00	SD2	CE2	HS6	GL11
4:25	SD3	CE3	HS7	GL12
4:50	SD4	CE4	HS8	GL13
5:15	End			
5:30	Business Meeting			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, October 16, 2002

8:30	J.-F. Berret (PL3)			
9:20	Coffee			
9:45	SD5	CE5	HS9	VP1
10:10	SD6	CE6	HS10	VP2
10:35	SD7	CE7	HS11	VP3
11:00	SD8	CE8	HS12	VP4
11:25	SD9	CE9	HS13	VP5
11:50	Lunch			
1:30	SD10	CE10	HS14	VP6
1:55	SD11	CE11	HS15	VP7
2:20	SD12	CE12	HS16	VP8
2:45	SD13	CE13	HS17	VP9
3:10	Coffee			
3:35	SD14	CE14	HS18	VP10
4:00	SD15	CE15	HS19	VP11
4:25	SD16	CE16	HS20	VP12
4:50	SD17	CE17	HS21	VP13
5:15	SD18	CE18	HS22	VP14
5:40	End			
6:00	Poster Session & Refreshments			

Thursday, October 17, 2002

8:05	SC1	IR1	HS23	SM1
8:30	SC2	IR2	HS24	SM2
8:55	SC3	IR3	HS25	SM3
9:20	SC4	IR4	HS26	SM4
9:45	Coffee			
10:10	SC5	IR5	HS27	SM5
10:35	SC6	IR6	HS28	SM6
11:00	SC7	IR7	HS29	SM7
11:25	SC8	IR8	HS30	SM8
11:50	SC9	IR9	HS31	SM9
12:15	End			

Session Codes

AS = Associating and Self-Assembling Fluids
CE = Coating and Extensional Processes
CF = Really Complex Fluids: Food and Consumer Products
FM = Non-Newtonian Fluid Mechanics and Instabilities
GL = Rheology of Glasses and Glass-Forming Liquids
HS = Heterogeneous Systems: Suspensions, Composite, and Multiphase Materials
IR = Interfacial Rheology: Adhesion and Slip
MR = Marrucci Symposium: Molecular Rheology of Concentrated Polymeric Systems
PL = Plenary Lectures
SC = Stiff Chains: Biopolymers, Polyelectrolytes, and LCPs
SD = Structural Development in Flow
SL = Jamming, Frustration, and Vitrification in Suspensions and Liquids
SM = Rheology at the Sub-Micron Scale
VP = Viscoelasticity of Polymer Liquids

Contents

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Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 University Ballroom PL1

Do we really understand the coil stretch transition and extensional stresses of polymer solutions?

Eric S. Shaqfeh
Department of Chemical & Mechanical Engineering, Stanford University, Stanford, CA

I will discuss three separate issues surrounding the coil to stretch transition in polymer solutions including: 1) Is the transition first or second order and when? 2) When the transition is second order in mixed flows, is it "sharp"? 3) Can we learn something about the entropic spring law by driving the transition and examining stress relaxation? To examine these issues, I will present a combination of recent Brownian dynamics simulations, filament stretching experiments, and single molecule visualizations to support conclusions concerning all three topics.

Symposium MR
Marrucci Symposium: Molecular Rheology of Concentrated Polymeric Systems

Organizers: Nino Grizzuti and Ronald Larson

Monday 9:45 Ballroom A MR1

Predicting the response of entangled linear polymers in transient complex flow using the multi-mode DCR model with chain stretch

Peter Wapperom[1] and Roland Keunings[2]
[1]Mathematics, Virginia Polytechnic Institute and State University, Blacksburg, VA; [2]CESAME, Division of Applied Mechanics, Universite catholique de Louvain, Louvain-la-Neuve, Belgium

In a recent paper [1], Ianniruberto and Marrucci have proposed a single-segment tube theory for entangled linear polymers that includes reptation, thermal and convective constraint release, and chain stretch. The resulting double-convection-reptation (DCR) model with stretch has the form of a double integral equation for the orientation tensor (which is approximated by a differential equation), and a differential evolution equation for the stretch. In a companion paper [2], the same authors have derived the corresponding multi-segment DCR theory. Using only two modes, the multi-segment theory already yields much improved predictions for the linear viscoelastic and shear response of monodisperse polymers. In this talk, we study by way of numerical simulation the response of the multi-mode DCR model in the start-up flow through an axisymmetric contraction/expansion geometry. We consider the single and two-mode models, using values of the constitutive parameters identified in [2] for a particular monodisperse polymer. The numerical technique is an extension of that used in our previous work [3] on linear and pom-pom polymers. We show that the differential approximation of the double integral DCR orientation model is indeed a good one, in contrast with that for the pom-pom model. We compare the one and two-mode DCR predictions and attempt to correlate them with the rheometrical response in shear and extension.

[1] G. Ianniruberto, G. Marrucci, J. Rheol., 45 (2001) 1305. [2] G. Ianniruberto, G. Marrucci, J. Non-Newt. Fluid Mech., 102 (2002) 383. [3] P. Wapperom, R. Keunings, J. Non-Newt. Fluid Mech., 97 (2001) 267.

Monday 10:10 Ballroom A MR2

Extensional stress growth, relaxation and capillary thinning in an entangled solution

Pradipto K. Bhattacharjee[1], Duc A. Nguyen[1], Gareth H. McKinley[2], and Tam Sridhar[1]
[1]Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia;
[2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA

We report an evaluation of the double constraint release model with chain stretch (DCR-CS), suggested by Ianniruberto and Marrucci, in predicting stress growth and stress relaxation behaviour of a well characterised entangled polymer solution in homogeneous uniaxial extensional flow. The DCR-CS model belongs to a family of models that incorporate constraint release, double reptation and segmental stretching into the basic reptation structure proposed in the original Doi-Edwards theory and seeks to extend the predictive capacity of the theory to complex flow fields. We show that the single mode, differential DCR-CS model performs well at intermediate to high stretch rates. The model also predicts the observed stress relaxation following the cessation of stretching. As the tensile stress in the filament decays, capillary thinning effects become increasingly important. We show that the DCR-CS model is also able to predict the gradual necking in the filament diameter that is observed experimentally.

Monday 10:35 Ballroom A MR3

Fluctuations in entanglements using a temporary network model with sliplinks

Jay D. Schieber
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A full-chain, temporary network model is proposed for nonlinear flows of linear, entangled polymeric liquids. The model is inspired by the success of a recent reptation model, but contains no tubes. Instead, each chain uses a different (and smaller) set of dynamic variables: the location of each entanglement, and the number of Kuhn steps in chain strands between entanglements. As before, the model requires only a single phenomenological parameter that is fit by linear viscoelasticity. The entanglements are assumed to move affinely, whereas the number of Kuhn steps varies stochastically from tension imbalances and Brownian forces. In the language of reptation, the model exhibits chain connectivity, chain-length fluctuations, chain stretching, and tube dilation. Because of the affinity assumption, the model should be expected to approximate well a linear chain in a matrix of fixed obstacles. Straightforward modifications to this assumption allow us to consider chains of any architecture in fluctuating obstacles (a network), or entangled chains in concentrated solutions or melts. A simulation algorithm for a simplified version of the model is described in detail, and some linear viscoelastic predictions are made. Finally, we make a few flow simulations and consider possible future generalizations of the proposed model, utilizing many of the physical ideas proposed by Marrucci and co-workers.

Monday 11:00 Ballroom A MR4

Topological gel - a real slip link model

Fumio Sawa[1], Takeshi Aoyagi[2], Jun-ichi Takimoto[3], and Masao Doi[3]
[1]Toshiba, Tokyo, Japan; [2]Asahi Kasei, Fuji, Japan; [3]Department of Computational Sciece and Engineering, Nagoya University, Nagoya, Aichi 464-8603, Japan

Topological gel is a new type of gel in which cross-links can slide along the main chains. To obtain the model of topological gel, polyrotaxanes modeled with end capped linear molecules and circular molecules were cross-linked. The circular molecules have one reactive site and can slide along the linear molecule. The chemical gel was also modeled by fixing the reactive site in the circular molecules to the nearest site in the linear molecule. Modeled gels (topological and chemical gel) were elongated uniaxially. It was observed that the topological gel has higher elastomeric property than the chemical gel at large elongation especially comparing to the chemical gel with phantom chains. It was confirmed that this wonderful properties of the topological gel is due to the "pulley-effect" which Itoh et al. suggested.

Monday 11:25 Ballroom A MR5

On the strain measure in entangled polymeric liquids

Francesco Greco
Institute for Composite Materials Technology (ITMC) – CNR, Napoli 80125, Italy

In entangled polymeric liquids, step deformation experiments are a key tool to investigate rheological properties. As it is well known, at sufficiently long times after a large step strain, these systems invariably show the so-called time-strain separability, i.e., factorization of the stress in a strain dependent factor, which is the Strain Measure Tensor, times a time-dependent "relaxation" function.

With the introduction of the reptation idea, and of the ensuing one-chain theories of polymer dynamics (Doi and Edwards, The theory of polymer dynamics, Clarendon, Oxford, 1986), a neat comprehension of the phenomena following a step strain has emerged at the molecular level, at least for systems made up of linear (monodisperse) chain molecules. Time-strain separability is seen to be a natural consequence of the "fast" rearrangement of a chain inside its cage, after the latter has been deformed, and of the "slow" reptative escape of the chain from the cage itself.

Doi and Edwards calculated a Strain Measure Tensor that is in good agreement with most of the available data, with no adjustable parameters, which is an impressive success of their theory. However, some discrepancies with experiments still remain, and also the theoretical arguments developed by them contain some approximations, which perhaps may be improved upon.

In a recent paper (Greco, Phys. Rev. Lett. 88 (2002) 108301), I presented a new Strain Measure Tensor. In the new calculation, it was instrumental to work within the Grand Canonical formalism of Statistical Mechanics, since a chain strand between two entanglements is in fact an open system, which exchanges monomers with its adjacent strands until an evenly equal chemical potential is established throughout. We will here present some extensions (in progress) of the original theory, dealing with i) the possibility of calculating the chemical potential itself, and ii) the possibility of adopting a non-Gaussian statistics for the strand between two entanglements.

Symposium FM
Non-Newtonian Fluid Mechanics and Instabilities

Organizers: Satish Kumar and Graham Harrison

Monday 9:45 Ballroom B FM1

Effects of the variation of the rheological parameters in polymer-induced drag reduction

Kostas D. Housiadas and Antony N. Beris
Chemical Engineering, University of Delaware, Newark, DE 19716

In this work we present a systematic investigation of the effects of viscoelastic flow parameters in polymer-induced drag reduction through (pseudo)spectral simulations of a turbulent viscoelastic channel flow. Viscoelastic effects are modeled by the finite-extensibility non-linear elastic dumbbell model with the Peterlin approximation (FENE-P) and the Giesekus model in order to better take into account the chain-chain interactions. The primary viscoelastic flow parameters are the friction Weissenberg number We_τ (a dimensionless relaxation time of the polymer in terms of the turbulent time scale), the molecular extensibility L for the FENE-P model, or the anisotropic mobility parameter α for Giesekus (where by setting $\alpha = L^{-2}$ the maximum extensional viscosity for the two constitutive models is the same), and the solvent to total viscosity ratio β. In contrast to previous work which was limited to low friction Reynolds number, the DNS are performed here for $Re_\tau = 395$, which is sufficiently high to allow for a full development of the near wall ($y+ < 100$) boundary layer. We will report results for three main series of runs to examine: (a) the effect of elasticity by varying $We_\tau = 0$, 25, 50, 87.5 and 125 at a constant L (or α) and β values, (b) the effect of the chain molecular weight by varying $L = 10$, 20 and 30 (or $\alpha = 1/100$, 1/400 and 1/900) at constant We_τ and β values and (c) the effect of the molecular concentration of the polymer by varying $\beta = 0.9$ and 0.99 at constant We_τ and L values.

Monday 10:10 Ballroom B FM2

Polymer chain dynamics in drag reducing flows: A multiscale approach

Vijay K. Gupta[1], Radhakrishna Sureshkumar[2], and Bamin Khomami[3]
[1]Chemical Engineering, Washington University, St. Louis, MO 63130; [2]Washington University, St Louis, MO; [3]Chemical Engineering, Washington University, St. Louis, MO 63130

The addition of polymer additives in a flow not only affects stability characteristics of the flow but also reduces drag [1-3]. It has been observed experimentally that even a very small amount (O (10) ppm) of polymer additives in a flow can reduce drag up to 70%. Though there have been a number of experimental studies on drag reduction by polymer additives, the numerical experimentations are limited. Sureshkumar et al. [4] were the first to perform direct numerical simulation (DNS) of the turbulent channel flow from first principles. In this study DNS simulations were performed with a kinetic theory based constitutive equation for the polymer, namely, the FENE-P elastic dumbbell model. Although many of the salient features of turbulent drag reduction were captured by this study, details regarding the specifics of polymeric chain orientation and it?s coupling to the flow kinematics were not extensively explored. In an attempt to understand this intricate coupling, we have performed Brownian Dynamics (BD) simulations of polymer chain dynamics with both Newtonian and FENE-P kinematics with kinetic theory based on single and multi-segment elastic dumbbell models for dilute polymeric solutions. Based on these simulations the connection between macromolecular dynamics and polymer induced drag reduction has been identified. Based on these finding we also have developed simple continuum and stochastic based phenomenological models of polymer induced drag reduction. In this presentation, the results of our chain dynamic simulations as well as the newly developed phenomenological models of polymer induced drag reduction will be discussed.

[1] J. L. Lumley, J. Polymer Sci.: Macromolecular Reviews, 7, 263(1973). [2] R. C. Vaseleski, A. B. Metzner, AIChE J, 20, 301(1974). [3] N. Berman, Ann. Rev. Fluid Mech., 10, 47 (1978). [4] R. Sureshkumar, A. N. Beris, R.A. Handler, Phys. Fluids, 9, 743 (1997).

Monday 10:35 Ballroom B FM3

Effects of polymers on models of the turbulent buffer region

Philip A. Stone and Michael D. Graham
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The key structural observation of drag-reducing polymer solutions is that the structures of the buffer region are modified. This region contains pairs of counter-rotating, streamwise vortices that lead to streaks in the streamwise velocity; these structures are based on a well-understood mechanism. To determine how the addition of polymer stress affects the mechanism, we study the effects of viscoelasticity on three-dimensional and quasi-two-dimensional (all three velocity components are non-zero but are only functions of the spanwise and wall-normal directions) flows in which the streamwise vortices are explicitly forced. The FENE-P dumbbell constitutive equation is used to calculate the polymer stress. The three-dimensionality of the flow is needed to produce the large polymer stretch necessary to modify the flow.

Monday 11:00 Ballroom B FM4

Stability analysis of multidimensional viscoelastic flows

Balraj Sadanandan and Radhakrishna Sureshkumar
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The stability characteristics of viscoelastic shear flows have been well documented in both inertial and purely elastic regimes. However, clear understanding of the stability characteristics of multi-dimensional viscoelastic flows is still lacking. Stability analysis of multi-dimensional flows requires significant CPU time and memory resources due to the non-availability of closed-form base state and the partial differential nature of the associated eigenvalue problem. We investigate the stability characteristics of the periodically constricted channel (PCC) flow of an Oldroyd-B liquid in the purely elastic regime. We examine the structure of the eigenspectrum in the limit of small channel wall amplitudes using a Mixed Collocation Galerkin Projection (MCGP) algorithm with the base flow computed using domain perturbation analysis (Sureshkumar, JNNFM, 97: 125 (2001)). The eigenspectrum consists of continuum set of eigenvalues, physically relevant mesh converged eigenvalues and mesh-dependent spurious eigenvalues. Systematic mesh refinement studies are performed to isolate the physically relevant eigenvalues (Sadanandan and Sureshkumar, JNNFM, 2002). For large channel wall amplitudes, the periodic expansion/contraction causes flow separation near the wall and large gradients in streamline curvature. In order to address these issues, we have developed a Chebyshev-Fourier Collocation (CFC) algorithm that uses staggered Chebyshev grid in the wall-normal direction and uniform Fourier collocation in the periodic direction. In the small wall amplitude limit the results are validated against those obtained from the MCGP algorithm. Results will be presented to illustrate the role of channel wall amplitude and frequency on the base flow and the linear stability characteristics. The use of Submatrix-based transformations of the linearized equations (SubTLE, Arora and Sureshkumar, JNNFM, 104: 75 (2002)) for reducing the CPU and memory requirements for the solution of the eigenvalue problem will also be discussed.

Monday 11:25 Ballroom B FM5

Stability analysis of polymer melt injection molding flows

Arjen C. Bogaerds, Martien A. Hulsen, Gerrit W. Peters, and Frank P. Baaijens
Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

Unstable flow conditions during injection molding of polymer products can result in severe restrictions on the process or the final product properties. Specifically, this instability can cause non-uniform surface reflectivity characterized by alternating shiny bands perpendicular to the main flow direction. This phenomenon is often referred to as `flow marks', `tiger stripes' or `ice-lines' and is observed for many polymer and polymer blend systems including PP, LDPE, ASA and PC/ABS blends. In order to be able to elucidate the mechanism of instability in this and other processing flows we first need to discuss the applied numerical algorithm. This linear stability analysis includes transient finite element calculations combined with a perturbation technique that incorporates the dynamic response of the free surface near the flow front to a disturbance in the flow. As the occurrence of the instability is largely dependent on the fluid rheology, the constitutive model that is used needs to be able to predict the necessary physics of the polymer melt. Here, we will apply the recently proposed eXtended Pom-Pom model to this flow. This model has shown to be able to accurately describe a number of polymer melts but it also allows us to independently alter the configuration of the representative Pom-Pom molecule and study its effect on the stability behavior of the flow.

Symposium AS
Associating and Self-Assembling Fluids

Organizers: Robert K. Prud'homme and Ralph H. Colby

Monday 9:45 Ballroom C AS1

Influence of multiple terminal hydrophobes on HEUR rheology

Peter T. Elliott and J. E. Glass
Polymers and Coatings Dept., North Dakota State Univ, Fargo, ND 58105

Narrow molecular weight, Hydrophobically-modified, Ethoxylated URethane (uniHEUR) type associative thickeners were synthesized with multi-branched terminal hydrophobes to determine their solution rheology. The hydrophobes, synthesized by the methoxide initiated polymerization of 1,2 hydrophobic epoxides, consisted of linear C10H25-, C12H25-, and C16H33- in groups or bunches of ~6 hydrophobes per multi-branch with the general structure CH3O[CH2CH(CxHy)O]6. These multiple hydrophobe bunches were coupled to the ends of 29,500 Mn poly(oxyethylene [POE]. Both anionic and nonionic surfactants affect viscosity increases with these HEURs, similar to our previous studies of other HEURs, with the larger hydrophobe HEUR displaying the greatest synergy with the nonionic surfactant. The difference between the influence of SDS and a nonionic surfactant is well highlighted in the oscillatory response with the [CH3O[CH2CH(C12H25)O]6-HDI]-HEUR670 where a dominant elastic modulus, *G*', is only seen with the nonionic surfactant. Flow profiles of the multiple branch HEURs in the presence of the optimum amount of SDS (6mM) display a transition from more newtonian flow to highly shear thinning, indicative of a yield stress, with increasing concentration. In the presence of the nonionic surfactant, NP-10, the shear profile is much different with multiple transitions and a high degree of thixotropy. Activation energies of flow increase with increasing hydrophobe size in the multiple branch structure, and there is a critical temperature (~5, 10, and 25oC for

the [CH3O[CH2CH(C10H21)O]6-, [CH3O[CH2CH(C12H25)O]6-, [CH3O[CH2CH(C16H33)O]6-, respectively) necessary to induce flow reflecting the relative strength and residence time of the hydrophobe in a micellar junction.

Monday 10:10 Ballroom C AS2

Rheology of associative polymers: Modulating hydrophobic interactions through inclusion compounds and surfactants

Ahmed A. Abdala[1], Rob English[2], and Saad A. Khan[1]
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The association of the hydrophobic segments of HASE associative polymers, comprising a comb-like architecture with a hydrophilic backbone and hydrophobes tethered to the backbone, is often exploited to obtain materials with enhanced solution viscosity and viscoelastic properties. While this enhancement attracts many technological applications, the ability to control the association and concomitant rheology is highly desirable. In this study, we modulate the rheology of HASE polymers through the interaction of the hydrophobic groups with α- and β-cyclodextrin (CD) and/or surfactants. The first part of the talk focuses on the use of the ring-shaped cyclodextrin with a hydrophobic core to encapsulate the hydrophobes of the polymer leading to a substantial change in rheology. Upon addition of a surfactant analogous to the hydrophobe of the polymer, a reversal in the rheology is observed as the cyclodextrins preferentially complexes with the surfactant. NMR measurements together with DSC are used to understand the interactions between the CD, surfactant and hydrophobes of the polymer and the resulting changes in rheology. In the second part of the talk, we focus on using a series of non-ionic nonyl phenol surfactants to mediate solution rheology. We find the hydrophile-lypophile balance of the surfactant to exert a strong influence on polymer rheology with behavior ranging from that of a low viscosity solution to that of an elastic gel. These results are interpreted in terms of the microstructures of the systems as observed from freeze fracture microscopy.

Monday 10:35 Ballroom C AS3

Association behavior of nonionic polyhedral oligosilsesquioxane (POSS) telechelics

Byoung-Suhk Kim and Patrick T. Mather
Chemical Engineering and Polymer Program, University of Connecticut, Storrs, CT 06269-3136

Self-assembly behavior of associative materials, such as block copolymers or hydrophobically modified polymers, has been extensively studied as a building block approach to the processing of nanostructured materials. We have investigated the association behavior of new amphiphilic telechelics incorporating polyhedral oligosilsesquioxane (POSS) as an end-group of poly(ethylene glycol) (PEG), which has a relatively narrow and unimodal molecular weight distribution (Mw/Mn

Monday 11:00 Ballroom C AS4

Block copolymers for the control of wax gelation in organic phases

Henry Ashbaugh and Robert K. Prud'homme
Chemical Engineering, Princeton University, Princeton, NJ 08544

The crystallization of waxes from oil phases can result in the formation of gels. These are a significant problem in the production of crude oil from off-shore wells. The addition of block copolymers that co-crystallize with the wax and provide steric stabilization of the resulting sturctures can prevent gelation.

Monday 11:25 Ballroom C AS5

Block copolymer self-assembly of nematic gels

Michael D. Kempe, Julia A. Kornfield, and Maria L. Auad
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Block copolymers with long side-group liquid-crystalline midblocks (>800 kg/mol) and LC-phobic end-blocks form a physical network that swells readily in an analogous small molecule LC to form nematic gels. Ultralong side-group liquid crystal polymers (SGLCP) are used for the midblock to enable gelation at relatively low concentration. In contrast to nematic gels made by a photo-initiated polymerization, the present gels have exceptionally uniform optical properties. Under an applied strain, an initially unaligned, polydomain gel aligns, creating a monodomain that is oriented well enough to generate clear conoscopic figures. In addition, these gels are amenable to various processing strategies for "printing" large area displays, since the physical crosslinks are reversible by addition of solvent or by increasing temperature. The transition temperature can be tuned by the choice of the end-blocks. The materials provide idea model systems in which the molecular weight between crosslinks is well defined and determined by the length of the polymer midblock. Using polymer-analogous synthesis we prepare SGLCPs with M up to 1,000,000 g/mol and Mw/Mn < 1.3. The synthesis and interactions of these SGLPs with an LC host are described first for homopolymers, examining the dramatic effects of molecular weight. At these higher molecular weights, we have measured a tumbling parameter less than negative one. Then we describe the phase behavior and electro-optic response of nematic gels formed using ABA block-copolymers.

Symposium CF
Really Complex Fluids: Food and Consumer Products

Organizers: Sumana Chakrabarti and Howard Barnes

Monday 9:45 Ballroom D CF1

The analysis of the frictional effect on stress-strain data from uniaxial compression of cheese

Maria Charalambides, Suk Meng Goh, and Gordon Williams
Mechanical Engineering, Imperial College of Science Technology and Medicine, London SW7 2BX, United Kingdom

Uniaxial compression tests were performed on Gruyere and Mozzarella cheeses in order to derive the true stress-strain curves of the cheeses. It was observed that shorter samples appeared stiffer when no lubrication was used, in agreement with many other published results on similar materials. This dependence on sample height was eliminated when a synthetic grease lubricant with polytetrafluorethylene (PTFE) was used. Therefore, the true stress-strain curves, i.e. free of frictional effects, were determined. Methods for reproducing these curves using data from unlubricated tests were then sought which was the main aim of the study. It was shown that the true stress-strain curves can be determined by testing samples of increasing heights until the difference between consecutive curves is negligible. The curve corresponding to the tallest sample can then be taken to represent the true stress-strain curve. If size or shape limitations do not allow testing of sufficiently tall samples, quadratic extrapolation of the results may be performed. Alternatively, an iterative finite element analysis could be used. The latter is a more accurate but more time consuming method than the extrapolation procedure. In addition it requires that the coefficient of friction is known. It was shown that the latter can be derived from an analytical scheme. These values of the coefficient of friction were approximately 0.1 for Gruyere and 0.3 for Mozzarella and they were in close agreement with numerical predictions.

Monday 10:10 Ballroom D CF2

Hierarchical investigation of factors influencing the rheological characteristics of milk fat

Geoffrey G. Rye, Jerrold Litwinenko, and Alejandro G. Marangoni
Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Texture is one of the major parameters of importance when considering consumer acceptability of fats and fat-based products. For this reason it is beneficial to understand and investigate the underlying physical parameters that affect the macrostructural properties of fats. This research demonstrates the relative effects of lipid composition, solid fat content (SFC), crystal polymorphism, microstructure, as well as nucleation and crystal growth kinetics on the mechanical properties of anhydrous milk fat (AMF) under varying processing conditions. AMF and AMF:Canola oil blends were cooled at rates of 0.1, 1 and 5ºC/min to 5ºC and stored for time periods of 1, 7 and 14 days prior to analysis. At a cooling rate (CR) of 0.1ºC/min SFC remained constant at 46-48% over the 14 day period, while higher CRs yielded values that were 5-10% higher. Crystal size and crystal network fractal dimension (D) values increased with decreasing CR. There was also evidence that polymorphic differences existed among the samples crystallized at different CRs, however, over time, all samples tended towards the B' polymorph. These parameters were then related to mechanical properties. Increases in CR yielded higher G' and yield force and decreased G'' and

tan δ values. AMF samples cooled slowly contained larger crystals, had a higher fractal dimension and had lower SFC, resulting in a softer fat, while faster cooling rates showed opposite relationships. A hierarchical structural model is proposed that accounts for the effects of structure on mechanical properties of edible fats.

Monday 10:35 Ballroom D CF3

Biaxial deformation of dough using the bubble inflation technique

Maria Charalambides[1], Leonard Wanigasooriya[1], Gordon Williams[1], and Sumana Chakrabarti[2]
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The bubble inflation test has been used to determine the equi-biaxial stress-strain curve of flour/water dough. This was achieved by undertaking experimental measurements of strain, wall thickness and radius of curvature at the pole of the bubble as well as pressure. It was observed that the bubble was spherical initially but changed to an elliptical shape at large strains. Bloksma's analytical procedure was used to calculate stress and strain at the pole from pressure and bubble volume data. It was found that the analytical strain was larger whereas the analytical pole thickness was much smaller than the experimental values. The bubble thickness distribution was more uniform than the analytical predictions. These discrepancies had a major effect in the analytical results, as both stress and strain were overestimated. The effect of the inflation rate on the accuracy of analytical models is also investigated. A numerical simulation of the inflation test was performed using Finite Element Analysis, in order to obtain further information regarding the accuracy of the analytical derivations. The effect of the chosen material model on the accuracy of the analytical model was investigated. The numerical results reinforced the conclusions drawn in the experimental study. Therefore, it is concluded that when the bubble inflation test is used, it is necessary that experimental readings of strain, thickness and height as well as pressure should be made to ensure accurate stress-strain curves.

Monday 11:00 Ballroom D CF4

Probing polymer interactions during dough fermentation with low intensity ultrasound

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Dough is an example of a really complex fluid, but one which has had a great deal of research effort directed at understanding its properties because of the importance of products that are processed from it. One tool capable of probing dough properties in a non-destructive manner is low- intensity ultrasound. Ultrasound (54 kHz) was used to monitor the fermentation of a dough that had been mechanically developed. Two headspace conditions during mixing were examined - ambient atmosphere and vacuum (0.13 atm). Ultrasonic velocity was substantially greater in the dough mixed under vacuum due to the presence of fewer gas cell nuclei in the dough. A substantial drop in velocity was observed during the first 20 minutes of fermentation for the dough mixed under vacuum. This could not be attributed to gas cell growth due to expansion by carbon dioxide because dough density (measured separately) changed only slightly during the same time period. It was surmised that as carbon dioxide was generated in solution, acidification of the dough increased the nett number of positive charges on the gluten polymer chains. Ionic repulsion between neighbouring gluten chains thus disrupted the hydrogen-bonding network within the dough, leading to the observed drop in velocity prior to gas cell development. The ultrasound technique thus proved useful for studying dough rheology, but it also further demonstrated the complex role that gluten proteins play in the dough system.

Monday 11:25 Ballroom D CF5

Interfacial rheology of microbubble contrast agents for medical ultrasound

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Intravenous encapsulated microbubble contrast agents (1-10 mu) have become an established clinical tool for enhancing ultrasound sensitivity. Bubbles enhance contrast due to their high scattering cross-sections relative to those of rigid particles. The high values result from the large difference in density and compressibility. Furthermore,

they act as damped mass-spring systems with enhanced resonant signal near their natural frequency. Most contrast agents are made with an encapsulating shell that prevents their premature dissolution. Free bubbles can last only a fraction of a second, whereas persistence requirements for a bubble to successfully reach from peripheral veins, where they are injected, to end-organs via heart is 12-27 seconds. Different contrast agents differ in the materials, structure and properties of their shells. We will present a comprehensive model of the surface rheology of the shell. It will be compared with the currently available models of the shell. Preliminary results of the encapsulated bubble dynamics will be provided.

Monday Afternoon

Symposium MR
Marrucci Symposium: Molecular Rheology of Concentrated Polymeric Systems

Organizers: Nino Grizzuti and Ronald Larson

Monday 1:30 Ballroom A MR6

A differential constitutive equation for entangled pom-pom polymers with CCR

Giovanni Ianniruberto
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A differential constitutive equation for entangled pom-pom polymers with CCR G. Ianniruberto Dipartimento di Ingegneria Chimica, Università Federico II, Napoli It is now well established that convective constraint release (CCR) is a key relaxation mechanism in fast flows of entangled polymers. Only when CCR is included in the classical Doi-Edwards theory for linear chains, predictions in fast flows are in good agreement with experiments [1-5]. We here propose a simple way of accounting for CCR in entangled branched polymers. Our starting point is the pom-pom model of McLeish and Larson [6]. Similarly to the original CCR theory for linear chains [1, 5], we account for CCR by simply modifying the orientational relaxation time of the pom-pom backbones. In doing so, we also propose a differential approximation of the pom-pom integral equation for backbone orientation, inspired by work done in [7]. Such a differential equation naturally predicts a nonzero second normal stress difference in shear, differently from the differential approximation originally proposed in [6]. This aspect, explicitly pointed out by Rubio and Wagner [8], partly motivated recent modifications of the pom-pom constitutive equation [9, 10]. Similarly to previous works, backbone stretch is described by an independent ODE.

[1] Ianniruberto, G. and G. Marrucci, J. Non-Newt. Fluid Mech. 65, 241 (1996). [2] Mead, D. W., R. G. Larson, and M. Doi, Macromolecules 31, 7895 (1998). [3] Ianniruberto, G. and G. Marrucci, J. Non-Newt. Fluid Mech., 95, 363 (2000). [4] Milner, S.T., T.C.B. McLeish, and A.E. Likhtman, J. Rheol. 45, 539 (2001). [5] Ianniruberto, G. and G. Marrucci, J.Rheol. 45, 1305 (2001). [6] McLeish, T.C.B. and R.G. Larson, J. Rheol. 42, 81 (1998). [7] Marrucci, G., F. Greco, and G. Ianniruberto, Rheol. Acta 40, 98 (2001). [8] Rubio, P. and M.H. Wagner, J. Rheol. 43, 1709 (1999). [9] Verbeeten, W.M.H., G.W.M. Peters and F.P.T. Baaijens, J. Rheol. 45, 823 (2001). [10] Öttinger, H.C., Rheol. Acta 40, 317 (2001).

Monday 1:55 Ballroom A MR7

Complex flow simulation of reptation based models with a stochastic strain measure and local variations of life span distribution

Piyush G. Gigras[1], Madan Somasi[2], and Bamin Khomami[1]
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In the years several new reptation models for polymer melts have been proposed which are based on the original Doi and Edwards reptation theory. The most sophisticated versions of this class of models are capable of predicting the rheology of entangled polymers with good accuracy. However with the new and better models comes the difficulty of simulating them efficiently in complex flows. In the last decade tremendous progress in development of efficient computation techniques for simulation of entangled polymeric systems in complex flow geometries has been made. Examples of such techniques are the Brownian Configuration Fields Method and the recently proposed Deformation Fields Method. However, these methods are restrictive to a certain class of reptation models and cannot be used to

simulate complex flow of the most advanced reptation based models. To overcome this shortcoming we have developed new multiscale simulation techniques that combine the essential features of the Brownian Configuration Fields Method and the Deformation Fields Method to allow simulation of advanced reptation models in complex flows. To illustrate the accuracy and computational efficiency of our computational technique, we have performed simulations with the recently proposed thermodynamically admissible reptation model of Ottinger in simple kinematics flows (plane shear and uniaxial extension) and have compared the results with pure Brownian dynamics simulations. We see an excellent agreement between the two. Complex flow calculations of various benchmark problems using this technique have also been performed and the results of these simulations will be presented.

Monday 2:20 Ballroom A MR8

Why does tube dilation work for stars?

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A simple but powerful treatment of constraint release invented by G. Marrucci is known as "Dynamic Tube Dilation". Its application to entangled branched polymers has been particularly successful, but on close examination, the reasons are mysterious. Here we take a closer look at cooperative retraction of branched polymers, and shed some light on recent experiments on dielectric relaxation, rheology and diffusion of star polymers.

Monday 2:45 Ballroom A MR9

Dynamics of star/linear polymeric systems

Dimitris Vlassopoulos[1] and Jacques Roovers[2]
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We study the linear melt rheology of mixtures of multiarm star and linear polymers; when the latter have molecular weight (M_l) much smaller than the star arm molecular weight (M_a), the linear chains act as macromolecular solvents, which dilute the entanglements of the arms. The full mechanical spectra of the mixtures of varying composition (and thus dilution) can be described using the Milner-McLeish theory and the high frequency Rouse modes. A universal description of the isofrictional arm relaxation time as function of the number of entanglements for stars of any functionality and degree of dilution is obtained. An additional slow structural mode, relating to the diluted colloidal star's hoping, also depends on the number of entanglements, but in a more complex way. When M_l increases and becomes comparable to M_a, a two-step plateau modulus is observed, bearing signatures of the linear chain and the star arm relaxations. We also explore the solution properties of the star/linear ternary systems. When dispersed in solvents of varying quality, the stars can undergo a glass-like gelation transition at a critical value of the effective volume fraction. We demonstrate that the addition of linear homopolymer chains of different sizes and concentrations reduces the modulus of the gel (for $M_l < M_a$) and eventually induces melting (for M_l comparable to M_a). We explain this kinetic transition in terms of effective interactions and star depletion, and discuss the role of solvent quality which is tuned via controlled temperature changes.

Monday 3:35 Ballroom A MR10

Quantitative prediction of linear viscoelastic properties for branched polymer melts using the hierarchical algorithm

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A recently developed "hierarchical algorithm" (Larson, 2001) generalizes the Milner-McLeish theory (1997) for branched polymers to allow for the effect of polydispersity and illustrates how information on branching can be inferred from rheology. However, because the early-time fluctuations were not considered, predictions of this algorithm are not in quantitative agreement with those of the Milner-McLeish theory. In this work we include the early-time fluctuations and compare theoretical predictions with experimental data for linear, star, star-linear blends, linear-linear blends, and combs of polybutadiene using two dilution exponent values, 1 and 4/3, in each case with the same values of plateau modulus (G_n), entanglement molecular weight (M_e), and equilibration time (τ_e). We use literature value of G_n, which have been obtained from linear viscoelastic data. We obtain the values of M_e and τ_e from fits to the experimentally-obtained zero-shear viscosities of linear and star polymers, which are available in the

literature. The hierarchical algorithm can predict well the linear viscoelastic properties of these well-defined branched polymers using the same values of parameters obtained from pure linear and star polymers. We also show how polydispersity in overall molecular weight and in the branch molecular weight affects the rheological properties of branched polymers.

[1] Larson, R. G., Macromolecules, 34, 4556 (2001). [2] Milner, S. T. and McLeish, T. C. B., Macromolecules, 30, 2159 (1997).

Monday 4:00 Ballroom A MR11

Rheology and molecular weight distribution of hyperbranched polymers

S Suneel[1], D. M. A Buzza[1], David G. Groves[1], T. C. B. McLeish[1], Dave Parker[2], Angela Keeney[2], and W. J. Feast[2]

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We study the melt rheology and molecular weight distribution of four short chain branched hyperbranched polyesters with different molecular weights and containing branched monomers of various alkyl chain lengths (*n* = 2 (ρ) 4). We find that the molecular weight distribution for all our samples obeys the static scaling form $n(M) \sim M^{-\tau} exp(-M/M_{char})$, where $n(M)$ is the number density of hyperbranched polymers with mass M, M_{char} is the largest characteristic molecular weight and τ the polydispersity exponent. The values of τ for all our samples (either 1.35 or 1.55) are close to but not the same as the mean field value of $\tau = 1.5$, a consequence of the fact that our polymers were synthesised under non-mean-field polycondensation conditions. For the materials with longer alkyl chain lengths (*n* = 3,4), we found that the rheology at low and intermediate frequencies could be modelled accurately using a dynamic scaling theory based on the Rouse model. This confirms that these hyperbranched polymers bahave as polymeric fractals which are essentially unentangled. For these polymers, the fractal dimension in the melt was determined to be $d_f = 3.0 \pm 0.5$, which is consistent with the hyperscaling relation $d_f = 3$ for hyperbranched polymers. For the materials with short alkyl chain lengths (*n* = 2), we found it necessary to include high frequency glassy modes in order to model the rheology at intermediate frequencies. This indicates that the glassy and Rouse modes are strongly coupled for short alkyl chain lengths so that it is no longer possible to obtain a good separation of timescales between the two modes.

Monday 4:25 Ballroom A MR12

Rheological investigation of the influence of short-chain branching on molecular order in melts of metallocene LLDPE

Ibnelwaleed A. Hussein

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The influence of molecular structure on molecular order (or disorder) of molten metallocene linear low-density polyethylene (m-LLDPE) will be studied by rheological methods. The effect of branch content and type on the molecular order in melts of m-LLDPE will be examined at temperatures in the processing range of polyethylenes (190^o-240^oC). Recently, Hussein and Williams (J. Non-Newtonian Fluid Mech., 86, 105-118, 1999) reported rheological evidence of molecular order in melts of linear PE similar to that of liquid-crystalline polymers. This study will extend the investigation to branched PEs. In this study, m-LLDPE will be used. The use of m-LLDPEs is expected to reveal fundamental understanding of the effect of branching, and isolate the interactions that are usually encountered in Ziegler-Natta LLDPE. The first-normal-stress-difference, and the steady-shear viscosity will be measured and monitored for anomalous behavior, especially at low shear rates. Anomalous behavior, if any, will be correlated to branch content and type. Hopefully, this basic study will result in some understanding of structure-order relationships in molts of branched PEs. Further, correlations between molecular structure and conformations, which are essential for the characterization of m-LLDPE, will be produced. Acknowledgement: Author would like to thank KFUPM for supporting this research project.

Monday 4:50 Ballroom A MR13

Prediction of dynamic moduli of low density polyethylene from chemistry and reactor conditions using architectural modeling

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The rheology of branched polymers is both fascinating for materials science and relevant for industry, since branches enhance the melt strength through extensional hardening. Understanding and predicting rheology from the branched polymer's molecular architecture has become possible through the recently developed tube models by McLeish et al. [1]. However, until now applications were restricted to architectures obtained from simplified chemical schemes with mono-dispersed segment lengths between branch points using the so-called "pom-pom" version of the model. For the case of ldPE we extended the rigorous version of the model to representative samples of a complete reactor population of molecular topologies with poly-disperse segment length distributions. Starting from chemical kinetics and reactor conditions (CSTR) we obtain molecular weight and branching distributions through a Galerkin finite element scheme. Subsequently CSTR populations of molecular architectures (thousands typically) are found using graph theory and Monte Carlo simulations [2]. The relaxation spectrum and the dynamic moduli are then calculated by an algorithm that screens all the architectures as represented in graphs in a time sequence. Processes such as arm retraction and dynamic dilution are taken into account within an extension of the inverted solution scheme of the Ball-McLeish equation [3] starting with the relaxation of the short arms at the shortest time scales and ending with the reptation of the longest segmental path within a molecule at the longest time scales. The relaxation spectrum thus found is very broad and possesses the same features as those obtained in experiment.

[1] Read, D.J., McLeish, T.C.B. Macromolecules 34, 2001, 1928-1945. [2] Iedema, P.D., Hoefsloot, H.C.J. Macromol. Theory Simul. 10, 2001, 870-880. [3] Larson, R.G. Macromolecules 34, 2001, 4556-4571.

Monday 5:15 Ballroom A MR14

Rupture of entangled polymeric liquids in elongational flow

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Polymer melts and concentrated solutions rupture at high rates of elongation in a manner that is reminiscent of the cohesive failure of solids and is distinct from necking ("ductile failure") and surface tension-driven breakup. The mechanism of this rupture is not understood. Reiner and Freudenthal proposed a dynamical theory of strength in 1938, which assumes that rupture occurs if the stored elastic energy exceeds the tensile strength of the liquid, which is itself an unknown parameter. A consequence of their theory is that the stress at rupture and the time to rupture are independent of the loading history and the rate of strain, both of which are inconsistent with experimental data. There has been little progress since this work.

We propose a simple molecular picture of rupture of a polymer filament at high elongation rates, in which catastrophic failure occurs when the frictional drag on an entangled chain can no longer balance the tension in the chain. The model, which is fully predictive and contains no adjustable parameters, captures the rupture characteristics of the available data sets, with quantitative agreement with critical stress-critical strain data and the dependence of critical strain on the Weissenberg number.

Symposium FM
Non-Newtonian Fluid Mechanics and Instabilities

Organizers: Satish Kumar and Graham Harrison

Monday 1:30 Ballroom B FM6

The stability of Taylor-Couette flows of Boger fluids with varying thermal sensitivity

James M. White and Susan J. Muller
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Viscous heating has been recently demonstrated through both theoretical and experimental studies (White and Muller 2002, Al-Mubaiyedh, et al. 2002) to dramatically affect the stability of Newtonian Taylor-Couette flow. The combination of viscous heating and centrifugal destabilization results in significantly lower critical Reynolds numbers and disturbance flows with different spatio-temporal symmetry than in isothermal Taylor-Couette flow. Here we present detailed experimental studies of the roles of centrifugal destabilization, thermal sensitivity of the viscosity, and the nonlinear behavior of the transition. We extend these experimental studies to a family of Boger fluids to probe the effects of viscous heating on the viscoelastic Taylor-Couette instability. Viscous heating is also predicted to have significant effects on the flow stability of viscoelastic fluids, where elasticity rather than inertia is the destabilizing influence, changing the disturbance flow from oscillatory and nonaxisymmetric to a stationary, axisymmetric flow. Boger fluids of varying thermal sensitivities of the viscosity are used to map the stability as a function of Deborah number and Nahme number. The experiments agree with the predicted features of the linear stability for an Oldroyd-B fluid; however the data for the different fluids do not collapse to a single, universal curve of De versus Na.

Monday 1:55 Ballroom B FM7

Non-monotonic flow of surfactant solutions in strain- and stress driven flow

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In the present paper, the flow properties of surfactant solutions in stress or strain driven shear flow are presented and discussed [1-2]. We focus on a specific surfactant solution that shows, in contrast to other solutions, a pronounced non-monotonic shear-thickening that is coupled with a transient rheo-chaotic flow behavior [1-3]. Under such conditions, a separation of the sample into two or several flow regimes is observed. In theses regimes either equal shear rate but different shear stresses or equal shear stress but different shear rates are present. Depending on the type of flow, stress- or strain-controlled, the rheological response functions of the solution differ once the rheo-chaotic flow regime is reached. The investigated solution exhibit stress oscillation (in strain-controlled experiment) or strain oscillation (in stress-controlled experiment) at a critical rate or stress. Due to the flow-induced orientation of structural elements such as wormlike micelles, non-monotonic flow is additionally coupled with flow instabilities caused by transient aggregation. The interaction between such shear induced structures and the rheometrical flow is discussed as driving mechanism of the observed flow phenomena. Detailed description of the non-monotonic flow of equimolar surfactant solutions is given elsewhere [1-3].

[1] Fischer P., Wheeler E. K., Fuller G. G.: Rheologica Acta 41 (2002) 35-44. [2] Fischer P.: Rheologica Acta 39 (2000) 234-240. [3] Wheeler E. K., Fischer P., Fuller G. G.: JNNFM 75 (1998) 193-209.

Monday 2:20 Ballroom B FM8

NMR study a the worm-like micellar aqueous solution CTAT in a capillary rheometer

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Experiments of Rheo-NMR were carried out to analyze the capillary flow behavior of a worm-like micellar aqueous solution of cetyltrimethylammonium tosilate at 30 °C. Two regions were studied with special interest, the contraction and the capillary region. The flow in the contraction region was surprisingly unstable even at very low shear rates. On the other hand, the velocity profiles along the capillary displayed a band near to the capillary wall, where an abrupt increase in velocity takes place for shear rates in the plateau of the non-monotonic flow curve. The width of this band increased radially for shear rates corresponding to the upturn in the flow curve. The observed unstable flow in the contraction region and the high shear rate band near to the capillary wall suggests that shear banding is the mechanism that drives the observed flow behavior.

Monday 2:45 Ballroom B FM9

Birefringence changes in the flow of spurting materials

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The birefringence changes in the capillary flow of spurting materials were studied in this work. Two different spurting materials were analyzed, a high-density polyethylene and an aqueous micellar solution of Cetylpyridinium Chloride. Variations in birefringence were detected and recorded by video images of the capillary cross section. In addition, light intensity was measured and stored in real time using a photodetector and an acquisition system coupled to a PC. The birefringence measurements were more sensitive and provided better information about the flow stability than pressure measurements. It is shown for both fluids that the only stable flow region is that before the onset of the spurt, then the flow is never stable again. Video images and the analysis of the signals related to the different capillary flow regimes are presented.

Monday 3:35 Ballroom B FM10

Stability and nonlinear dynamics of film blowing

Hyunchul Kim, Hyun W. Jung, and Jae C. Hyun
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Nonlinear dynamics of film blowing process has been studied focusing on stability and transient behavior of the system. The governing equations consisting of two well-known force balances and a Phan-Thien Tanner constitutive equation have been solved using a newly-devised numerical scheme which incorporates an orthogonal collocation with finite elements, to yield transient solutions of the film blowing operation which are hitherto difficult to obtain due to severe numerical stability problems when the system is in instability called draw resonance. Thus obtained simulation results make possible more systematic analysis of draw resonance: firstly, the same draw resonance criterion based on the traveling times of kinematic waves on the free surfaces, originally derived from spinning process and later confirmed for film casting, again has been found to equally hold for this film blowing, and secondly the effects of fluid viscoelasticity and aspect ratio of the blowing machine on the stability have been investigated on both extension-thickening and extension-thinning fluids.

Monday 4:00 Ballroom B FM11

Draw resonance in a fiber spinning process: Model predictions using linear stability analysis

Antonios K. Doufas, Madan Somasi, and Joey Storer
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Flow instabilities pose a major impediment in high-throughput industrial processes. In the absence of robust and accurate modeling tools, a large amount of expensive and time-consuming experimental work is often necessary to determine the right set of process conditions for stable operation. Furthermore, several scale-up issues have to be resolved before the application can be commercially successful. In this study, we present a modeling capability that can be used to perform dynamic analysis of fiber spinning process in order to predict the fabrication conditions and material properties under which draw resonance occurs. Our approach addresses the coupled effects of viscoelasticity and flow-induced crystallization on fiber instabilities, while traditional approaches neglect the critical effects of crystallization. The two-phase constitutive/microstructural formulation of Doufas et al. [1,2] and the pom-pom constitutive equation [3] have been incorporated in our analysis. Our development is based on a linearized

perturbation analysis using a normal mode expansion method to study the effects of small disturbances in the spinline around the steady state. Comparisons of the model predictions with rheotens force - draw ratio curves will be discussed.

Relevant external publications: [1] A. K. Doufas, I. S. Dairanieh, and A. J. McHugh, "A continuum model for flow-induced crystallization of polymer melts", J. Rheology, 43 (1999), 85-109. [2] A. K. Doufas, A. J. McHugh, and C. Miller (DuPont), "Simulation of melt spinning including flow-induced crystallization. Part I. Model development and predictions", J. Non-Newtonian Fluid Mechanics, 92 (2000), 27-66. [3] N. Inkson and T. C. B. McLeish, "Predicting low density polyethylene melt rheology in elongational and shear flows with "pom-pom" constitutive equations", J. Rheology, 43 (1999) 873-896.

Monday 4:25 Ballroom B FM12

Effect of upstream boundary conditions on the stability of fiber spinning in the highly elastic limit

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

We consider fiber spinning for the upper convected Maxwell fluid in the limit of high Deborah number. We compare several choices of boundary conditions which may be imposed. In addition to the takeup speed and the upstream flow rate, we consider four different boundary conditions: the upstream velocity, upstream elastic stress, the force in the fiber, and the ratio of stress to the square of the velocity (the latter can be motivated by a limit of vanishing retardation time). We find that the effect of the boundary condition on stability is crucial; in one case we even find an instability even though the draw ratio is 1.

Monday 4:50 Ballroom B FM13

Flow through tubes of two immiscible liquids with different rheological behaviors

Edson J. Soares, Marcio S. Carvalho, and Paulo R. Souza Mendes
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There are a number of industrial processes which involve the displacement of a liquid in a tube by another. One example is the cementing operation of petroleum wells, when the drilling fluid is displaced by a length of washing fluid, which in turn is pushed by the cement paste. In this flow, it is important that little or no mixing at the interfaces is assured, to avoid contamination of the cement paste by the other fluids. Therefore, prediction of the interface shape as a function of the governing parameters is in order. In this work we obtained numerical solutions for the laminar flow of a Newtonian liquid displacing a viscoelastic liquid in a tube. The finite-element method has been employed, and part of the solution obtained was the interface shape and position. We obtained solutions for different combinations of values of the Capillary number, viscosity ratio and Reynolds number. We also performed flow-visualization results for water-based solutions of PEG/PEO displacing a Newtonian vegetal oil and vice-versa. The results obtained are presented in the form of interface shapes and streamlines.

Monday 5:15 Ballroom B FM14

Comprehensive constitutive model for the prediction of stresses in immiscible blends

Abdulwahab S. Almusallam, Ronald G. Larson, and Michael J. Solomon
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We report a comprehensive constitutive equation that can describe the convection, retraction, breakup and coalescence of single droplet and blends of immiscible Newtonian components. The model is comprehensively tested by comparison to literature and experimental data collected under a variety of conditions. At situations where the strain rate is below the critical value for break-up, the model shows good agreement with literature data for single droplet deformation at different flow types. Droplet breakup is accounted for by a term that matches the time evolution of anisotropy as predicted by the Tomotika theory for the capillary breakup of an elongated cylinder. Breakup experiments of elongated single droplets were carried out to test the breakup part of the model, and good agreement was found, particularly for highly extended droplets. In start-up of strong shearing, the comprehensive constitutive model predicts the transient shear and first normal stress difference qualitatively, but quantitative agreement is lacking, apparently due to the ad hoc way that the model droplet retraction part is combined with that of droplet breakup and perhaps also due to concentration effects. However, the combined model predicts a steady-state droplet size that is inversely proportional to shear rate in the start-up of strong shearing, in agreement with theoretical predictions dictated by the critical capillary number for breakup.

Symposium AS
Associating and Self-Assembling Fluids

Organizers: Robert K. Prud'homme and Ralph H. Colby

Monday 1:30 Ballroom C AS6

Network formation and sieving performance of self-assembling hydrogels

Rob Lammertink and Julia A. Kornfield
California Institute of Technology, Pasadena, CA

Self-assembling hydrogels have been synthesized and studied for use as sieving media in capillary gel electrophoresis applications. In order to fill capillaries and microchannels with self-assembling solutions, their rheological behavior is of extreme importance. To meet the requirement for materials with tunable rheology and sieving characteristics, we explore fluoroalkyl ended poly(ethylene glycols) that form networks in water via aggregation of the hydrophobic end groups. These hydrogels are extremely interesting for applications in need of hydrogel materials that suffer from difficulties during processing. More specifically, entangled polymer solutions that are frequently used as sieving media in capillary electrophoresis poses extremely high viscosities and therefore require high pressures to be transported into small capillaries and channels. We examine the effects of PEG length and fluoroalkyl length on rheological properties and separation performance for DNA electrophoresis.

Monday 1:55 Ballroom C AS7

Tuning the linear viscoelastic behavior of wormlike micelles through polymer-surfactant interaction

My Hang T. Truong and Lynn M. Walker
Dept. Chemical Engineering, Carnegie Mellon University, Pittsbrugh, PA 15213

In this work, nonionic additives are used to tune the linear viscoelastic behavior of aqueous semidilute wormlike micellar systems of cetyltrimethylammonium p-toluenesulfonate (CTAT). By varying the length of these slow-breaking micelles (defined in the context of the theory developed by Cates) and their degree of entanglement, mixed systems offer more precise control of the rheology than pure CTAT systems. For example, polyethylene oxide (PEO) enhances the terminal viscosity of the CTAT system, while the number of entanglements per micelle remains constant. Increasing the concentration of CTAT also has the same effect on the viscosity, but the degree of entanglement increases dramatically. Through binding and comicellization, hydroxypropylcellulose (HPC) and block copolymers of ethylene oxide and propylene oxide (Pluronic copolymers) cause the formation of shorter micelles. As such, these mixed systems have lower viscosities and degrees of entanglements, yet the viscoelastic behavior remains qualitatively similar to the original CTAT system. The interactions of these polymers with CTAT allow for modifications of the micellar structure without changing the volume fraction of micelles, thus creating rheological behavior, which cannot be achieved in pure CTAT systems.

Monday 2:20 Ballroom C AS8

Headgroup effect on drag reduction and microstructures of quaternary ammonium surfactants

Ying Zhang[1], Yunying Qi[1], Yeshayahu Talmon[2], and Jacques L. Zakin[1]
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It is known that some quaternary ammonium cationic surfactants mixed with certain counterions reduce pressure drops in turbulent flows. Usually, the solution is viscoelastic. Trimethylammonium cationic surfactants with an alkyl chain length of 16 to 22 are one of the most widely used drag reducing types. When mixed with appropriate amounts of anionic counterions, usually sodium salicylate (NaSal), they self assemble to form micelles. Both rheological and microstructural studies of these drag reducing solutions indicate the existence of long thread-like micelles, with properties similar to polymer chains.

In this study, two unusual quaternary ammonium surfactants were investigated, cetyldimethylethylammonium bromide and benzyldimethyl (hydrogenated tallowalkyl) ammonium chloride. Substitution of the bulky ethyl and phenyl groups for one of the three methyls leads to a larger headgroup area and therefore smaller packing parameter at the same alkyl chain length, which tends to shorten thread-like micelles. Drag reduction, rheological, microstructure and ^{1}H NMR studies of these two surfactants with different counterion to surfactant ratios were carried out and compared to those of trimethylammonium salts with comparable alkyl chain length.

Monday 2:45 Ballroom C AS9

Shear induced multilamellar vesicles

Bing-Shiou Yang, Robert K. Prud'homme, and William B. Russel
Chemical Engineering, Princeton University, Princeton, NJ 08544

Surfactant solutions which form lamellar phases can be sheared to produce multilamellar vesicles. We show that the addition of hydrophobically modified polymers to these phases enhances the formation of multilamellar vesicles and enhances their stability. The utility of these formulations will be discussed.

Symposium SL
Jamming, Frustration, and Vitrification in Suspensions and Liquids

Organizers: Charles Zukoski and Jennifer Lewis

Monday 3:35 Ballroom C SL1

Optical rheology studies of the formation and aging behavior of soft glassy clay particle suspensions

Virgile Viasnoff[1], Laura Collins[2], David Sessoms[2], Brian Chung[2], and James L. Harden[2]
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Studies of the collective dynamics and microrheology of aqueous suspensions of Laponite, a synthetic Hectorite clay composed of charged, nanoscopic discoid particles, will be presented. Laponite suspensions form soft transparent colloidal glasses at low particle concentrations. In the glassy phase, Laponite suspensions have novel rheological and aging properties. Diffusing wave spectroscopy was used to investigate the sol-glass transition and the linear viscoelastic properties of these colloidal suspensions as a function of clay concentration, pH, and sample age by monitoring the thermally-induced fluctuations of added tracer particles. The formation and aging of the soft glassy phase occur in two distinct stages. The viscoelastic behavior of the glassy state is characterized by novel power-law creep behavior with an exponent that approaches zero with increasing concentration or sample age, followed by a long-time collective relaxation. The creep exponent for samples of different age or Laponite concentration can be rescaled onto a single mastercurve in both the formation and aging regimes, indicating universal behavior for glassy dynamics in this system. In response to shear-induced liquification, samples prepared at high pH recover their glassy behavior after a characteristic induction period. In contrast, samples prepared at lower pH do not exhibit such rejuvenation behavior. These results will be compared with recent models of the rheology and aging of soft glassy materials.

Monday 4:00 Ballroom C SL2

Colloidal inks for directed asssembly of 3-D periodic structures

J E. Smay and Jennifer A. Lewis
Materials Science & Engineering and Chemical Engineering, University of Illinois, Urbana, IL 61801

Colloidal assembly of mesoscale periodic structures requires control over, and, hence, a fundamental understanding of interparticle forces, phase behavior, and structure evolution during fabrication. Such structures have been fabricated via directed assembly of colloidal inks. Concentrated colloidal gels with tailored viscoelastic properties

were designed to form self-supporting features. The inks were deposited in a layer-by-layer sequence to directly write the desired 3-D pattern. Periodic structures with spanning features that vary between ~ 100 mm and 1 mm were assembled. Rheological measurements were carried out to characterize the flow behavior and elastic properties of concentrated inks of varying gel strength. Deflection measurements of spanning elements were used to probe the relationship between gel strength, deposition speed, and shear rate profiles in the nozzle. These observations revealed that the ink adopted a rigid (gel) core-fluid shell architecture during assembly, which simultaneously facilitated bonding and shape retention of the deposited elements.

Monday 4:25 Ballroom C SL3

Scaling in the dynamics of jammed attractive colloids

Veronique Trappe[1], Hugo Bissig[1], Roland Keir[1], Vikram Prasad[2], Sara Romer[3], Peter Schurtenberger[1], and David A. Weitz[2]
[1]University of Fribourg, Fribourg, Switzerland; [2]Harvard University, Cambridge, MA; [3]Department of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom

Jammed attractive colloids are found to exhibit a remarkable scaling behavior in their dynamical and rheological properties. This scaling behavior appears to be nearly independent of the particle volume fraction and the strength of the attractive interaction between the particles. We discuss this finding within the framework of a recently proposed jamming state diagram, where the intrinsic control parameters to and within the jammed state are the density, the temperature and the mechanical load applied on the system.

Monday 4:50 Ballroom C SL4

Dense suspensions of colloidal particles under shear flow

Georgios Petekidis[1], Dimitris Vlassopoulos[1], and Peter N. Pusey[2]
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The Rheological behaviour of colloidal glasses subjected to oscillatory shear strain is studied by the techniques of Light Scattering Echo (LS Echo) and rheology. LS Echo directly follows the motion of the particles through peaks (echoes) in the intensity autocorrelation function; the height of the peak measures the reversible motion in the sample. Monodisperese and polydisperse hard sphere PMMA particles were studied at several volume fractions in the glass regime. The latter system was used to avoid crystallization under shear and allow the study of shear-induced rearrangements in the absence of an ordering transition. The yielding behaviour was monitored through the irreversible particle rearrangements as a function of frequency and strain. At high volume fractions, the glasses were found to yield at strains as high as 15%. The nature of the yielding process depends strongly on concentration. At high volume fractions irreversible rearrangements increase rapidly as strain amplitude is increased whereas at lower volume fractions a more gradual yielding was observed. Such complicated behaviour results from a combination of three effects: an elastic distortion, as measured by rheological experiments; a reversible viscous distortion; and a high concentration analogue of Taylor dispersion arising from the interplay of Brownian motion and Stokes flow. Step stress (creep) tests and dynamic strain sweeps provided complementary information of the viscoelastic response of the glasses.

Monday 5:15 Ballroom C SL5

Aging, structural evolution and non-linear rheology of thermoreversible colloidal gels

Priya Varadan, Ali Mohraz, and Michael J. Solomon
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The rheology of colloidal particulate gels is characterized by the existence of an apparent yield stress, solid-like linear viscoelasticity, aging and an extreme dependence of the measured stress on prior deformation history. Fielding et al. (Journal of Rheology, 44 323 2000) have recently reported predictions of a model of the rheology of soft glassy materials (Sollich et al., Phys. Rev. Lett. 78 2020 1997) that qualitatively account for many of the aforementioned phenomena. We experimentally investigate implications of this soft glassy rheology (SGR) model for colloidal particulate gels by studying a thermoreversible system of organophilic silica suspended in the solvent hexadecane. Gelation in this system has been shown to display features common to the glass transition of amorphous materials (Solomon and Varadan, Phys. Rev. E, 63 051402-1 2001). Thermoreversible gelation allows the prior deformation history of the suspension to be precisely controlled, which is ideal for aging studies. We report creep measurements of the suspensions that quantify the effect of aging time on the measured compliance. Characterization of linear viscoelasticity also allows SGR model parameters to be estimated, which can in turn be used to analyze measurements of creep in the non-linear regime, particularly as they relate to the existence of the yield stress. We assess the possible implications of slip of the gel body during deformation. The observed rheology is discussed in light of small-angle light scattering and confocal laser scanning microscopy studies of the same thermoreversible system.

Symposium CF
Really Complex Fluids: Food and Consumer Products

Organizers: Sumana Chakrabarti and Howard Barnes

Monday 1:30 Ballroom D CF6

The application of rheological thermal analysis to foods

Mahesh Padmanabhan
Basic Sciences, Kraft Foods, Glenview, IL 60025

The technique of rheological thermal analysis (traditionally known as DMA or DMTA), commonly used with polymers, is a powerful rheological technique for foods. The technique involves measuring the rheological properties as a function of temperature through the use of linear or stepwise change of temperature, akin to DSC. This technique has gained some attention in the food area. Both fundamental (structural) and practical (functional) information can be obtained using this technique. Use of rheometers equipped with convection oven allow the collection of data over a wide range of temperatures and monitor various rheological events such as glass transition, melting transition, crosslinking reactions, etc. Conventional and non-conventional uses of this technique for foods will be provided through illustrative examples.

Monday 1:55 Ballroom D CF7

Sealant, a complex commercial fluid

Chris C. White and Don Hunston
Building Materials, NIST, Gaithersburg, MD 20899

Polymeric sealants are complex materials with both solid and fluid characteristics. They are an important example of a major consumer product where the performance depends critically on their rheological and adhesive properties. At first look, these materials appear to be simple elastic solids, but upon further examination, the behavior becomes increasing more complex. For example, testing of a model sealant indicated that the first elongation shows remarkably different properties than those obtained on any subsequent elongations similar to the Mullins effect. Moreover, the response showed a clear dependence on both time and strain level which can only be represented with a non-linear viscoelastic model. On the other hand, detailed characterization suggests that the behavior may not be quite as intractable as it first appears. After the first elongation, subsequent deformations show quite reproducible behavior so long as the maximum strain level in the initial elongation is not exceeded. When this reproducible behavior is examined over the range of conditions usually tested, the non-linearity and time dependence are modest, and the response is largely elastic. Moreover, there are indications that the non-linearity and time dependence may be separable. These points will be examined with data from several sealant samples with different chemistries.

Monday 2:20 Ballroom D CF8

The effect of rheology on printing performance of piezo inkjet inks

Caroline M. Ylitalo
Advanced Materials Technology Center, 3M Company, St. Paul, MN 55144-1000

Several model systems were used to develop fundamental understanding of the influence of materials properties (surface tension, viscosity, and elasticity) on the printing performance of piezo inkjet inks. Using a simple energy

balance equation, it was found that the rheological properties of inkjet inks are the most important factors in determining ink jettability (is it going to print from the desired printhead?) and ink performance (does the ink drop ejected from the printhead have sufficient kinetic energy to land in the desired location?).

Monday 2:45 Ballroom D CF9

Rheological characterization and modeling of aqueous guar gum solutions

Marco Dressler, Peter Fischer, Daniel Renggli, David Vinzce, and Erich J. Windhab
Institute of Food Science, ETH Zurich, Zurich 8092, Switzerland

The rheological properties of aqueous guar gum solutions have been investigated for different concentrations and temperatures in a cone-and-plate rheometer. Focussing on the shear stress and on the first normal stress difference, we found for low shear rates a monotonous increase of the stresses as a function of time, whereas at higher shear rates a pronounced overshoot in the transient stresses has been detected. The steady state values of the shear viscosity and the first normal stress coefficient as a function of shear rate reveal the characteristic shear-thinning behavior. It will be shown whether the solutions behave thermorheologically simple, i. e. whether the time temperature superposition principle can be adopted to describe their rheological behavior at different temperatures. Furthermore, constitutive equations for the extra stress tensor will be adopted to describe the measured data. Several models of polymer rheology such as the differential Giesekus and the PTT Model will be solved for transient and steady state conditions and the results will be compared with the measured data.

Monday 3:35 Ballroom D CF10

Interfacial shear rheology of milk proteins at the oil/water interface

Philipp Erni and Peter Fischer
Institute of Food Science, ETH Zurich, Zurich 8092, Switzerland

The flow of fluids composed of immiscible mixtures of two or more phases is of interest in a wide range of research fields, such as foods, polymers, pharmaceuticals and cosmetics. Amphiphilic molecules such as surfactants or proteins are used to produce and stabilize such products. By adding such surface acting components one is potentially able to alter the physical and chemical properties (viscosity, elasticity, surface tension) of the interfaces [1, 2]. In particular, the rheology of the interfacial film has a significant influence on emulsifications, emulsion stability, foam stability and de-foaming. In the present work, we focus on the rheology of different milk proteins at the planar liquid-liquid interfaces. Using a biconical geometry that is situated at the oil-water interface the steady state as well as the transient interfacial shear viscosity is investigated. Finally, the adsorption behavior of different proteins such as compact globular and less structured molecules at different bulk phases is presented and discussed.

[1] Fischer P. et al.: Langmuir 16 (2000) 726. [2] Fischer P.: Proceedings 2nd ISFRS (2000) 149.

Monday 4:00 Ballroom D CF11

The rheology of model ice cream systems

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This paper is concerned with the rheology and microstructure of a model ice cream system. Ice cream consists of a rheologically complex matrix together with air and ice inclusions. This highly complex product was simplified into a model system containing hard spheres to mimic the ice crystals phase, and gas cells to mimic the air phase. The volume fraction was systematically manipulated, and the effect on the overall properties observed. A model ice cream matrix was developed that had a similar rheological behaviour to edible ice cream. A controlled stress rheometer was used to characterise the base rheology of the matrix and of the matrix with solid inclusions and air as foam. Significant low shear viscosity enhancement was established and a Krieger Dougherty type relation fitted the data reasonably well. High shear rheology measurements were made using a recently developed multipass rheometer (MPR) [Mackley et al. (1995)]. This data revealed a high shear rate plateau for the matrix and interestingly showed that with the addition of foam, the apparent viscosity of the composite fluid fell below that of the matrix. This result can be interpreted in a similar way to Thompson (2001), who observed a similar effect for low viscosity emulsion drops in a viscoelastic matrix. Finally, optical observations of the shear behaviour of the foamed composite revealed an interesting chaining and coalescence effect that produced extended air threads in the fluid.

Monday 4:25 Ballroom D CF12

Texture profiling with the vane: A general method for characterizing shear-sensitive soft matter

Alan Parker
Research Division, Firmenich SA, Meyrin 2 Geneva CH-1217, Switzerland

Measuring the rheological properties of shear sensitive soft matter poses severe methodological problems. The key problem is that placing the sample in the measurement geometry partially destroys the structure that we want to characterize. I argue that the vane geometry is the **only** solution to this problem. In consequence, we have to learn to live with the problems of interpretation and calibration that its use imposes. In fact, for many practical applications the disadvantage of only obtaining relative values is far outweighed by the advantages of rapid, low cost "in situ" measurements.

The rheology of soft matter combines elements of viscoelasticity, thixotropy, yield and fracture. Therefore, a single experimental protocol can never unambiguously define a sample's properties. Nevertheless, I demonstrate that an overshoot measurement is often sufficient for applications in quality control and product development. In doing so, I show that the common identification of the maximum in the overshoot curve with the yield stress is only valid under restricted conditions. In general, it is better interpreted using the Maxwell-Quemada thixoelastic model.

When more complete characterization is required, three protocols can be used to supplement the standard overshoot measurement: 1) Overshoot and stress relaxation at a range of rotation rates; 2) Stress growth and relaxation for times before that of the stress maximum, 3) Creep at a ranges of stresses below the maximum. The creep curves often oscillate, so data fitting requires the use of dashpot and spring models incorporating the inertia of vane + sample.

Use of the technique is illustrated with data from a range of food and consumer products.

Monday 4:50 Ballroom D CF13

The rheology and microstructure of structured fluids

Jason R. Stokes and Julia H. Telford
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Structured fluids, or semi-solids, shear thin dramatically at a critical shear stress and include materials such as skin creams and lotions, sauces, pastes, spreads, mayonnaise, and ice cream. Such fluids also tend to be highly thixotropic such that rheological measurements are often irreproducible due to the disruption of the microstructure during sample loading. The use of a vane, consisting of four blades that form a cross shape at the end of a central shaft, inserted into the fluid is an easy and convenient method of performing accurate rheology measurements of such samples. The vane enables the flow curves to be measured for structured fluids, which would otherwise be difficult or impossible to determine accurately using conventional techniques. In particular, example studies have shown that crucial textural attributes of mayonnaise can be distinguished using a simple rapid test on the sample in the jar. When carried out using more conventional rheological techniques the structure is broken down during sample handling, removing the differences observed in the vane test. The yielding and flow behaviour of ice-slurries is also investigated using this method at sub-zero conditions. Problems associated with sample loading and wall slip, as well as accretion of ice on shearing surfaces, which make conventional rheology all but impossible, are avoided. Accurate rheological measurements have also allowed the examination of structured fluids in terms of their underlying microstructure.

Monday 5:15 Ballroom D CF14

Rheological characterization of weekly structured food samples

Joerg Laeuger, Simone Will, and Klaus Wollny
Physica Messtechnik, Stuttgart D-70567, Germany

Food products are rather complex systems. Due to stability reasons a structure is often highly desirable. On the other hand, since a good mouth feeling is required, these structure are mostly very week and are influenced at already very small stresses and strains. A new oscillation method (Direct Strain Oscillation - DSO) based on a real position control was recently introduced which extends the measuring range of a commercial rheometer to torques as low as 0.02 μNm (Rheol Acta 2002, to be published). Another feature of the DSO method is the absence of even the slightest additional rotational drift which might destroy a week structure. The DSO method was now used to measure the structure of low viscous milk drinks, starch dispersions, and chocolate samples. Strain sweeps showed large differences between three commercial milk drinks. An oscillatory test with constant amplitude and constant frequency immediately following an interval with a constant high shear rate enabled the determination of the structure recovery, i.e., the thixotropy. In order not to influence the structure during the rebuilding process the constant amplitude needs to be within the linear visco-elastic range of the samples. Even for the sensitive double gap geometry used the resulting instrumental torques are smaller than 0.1 μNm and therefore significantly lower as attainable before. Starch dispersions with different concentrations were investigated with oscillatory tests. Strain and frequency sweeps showed that at very low concentrations very small stresses need to be resolved in order to measure in the linear visco-elastic range. As a third example measurements on chocolate melts at 40°C are presented. As most commercial food samples chocolate exhibits an extremely narrow linear visco-elastic range. Results of strains sweeps on different chocolates samples are shown which indicate the complex structure of theses samples. The different samples have a different but reproducible behavior after leaving the linear range in the strain sweeps.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 University Ballroom PL2

Tubes and slip links: Two views of entangled polymer rheology

Ronald G. Larson
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Since the first theories were developed over 30 years ago, entanglements have been visualized using the "slip link" and the "tube" models, with most theoretical developments based on the latter. By inclusion of not only reptation and primitive path fluctuations, but also constraint release phenomena, using the tube model, quantitative predictions of the linear viscoelasticity of monodisperse and polydisperse linear polymers has become possible in recent years. Increasing attention is therefore being paid to long-chain branched polymers, especially those with multiple branch points, for which a theory for the motion of a branch point through a non-permanent entanglement mesh is required, but still mostly lacking. The growing complexity of adding further extensions to the tube model has re-awakened interest in the old slip link model as an alternative for describing entanglements. Ensembles of chains with slip links, which can now easily be simulated by computer, can capture fluctuation and constraint-release phenomena more simply and self-consistently than can tube models. We are thereby gaining new insights into fluctuation effects and even how branch points move in entangled polymers.

Symposium MR
Marrucci Symposium: Molecular Rheology of Concentrated Polymeric Systems

Organizers: Nino Grizzuti and Ronald Larson

Tuesday 9:45 Ballroom A MR15

Complex fluid interfaces

Gerald G. Fuller
Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Complex fluid interfaces are ubiquitous in industrial and living systems. These deformable surfaces are laden with amphiphiles and are highly structured. Common examples include the phospholipid bilayer of the cell wall and emulsion droplets stabilized with block copolymers. The flow response of these systems is highly nonlinear and nonNewtonian. This paper presents experimental methods that can access both the mechanical and microstructural properties of this fragile surfaces. Applications include two-dimensional liquid crystals, simple fatty acids, and two-dimensional suspensions.

Tuesday 10:10 Ballroom A MR16

Rigid rod probes of concentrated polymeric solutions

Paul S. Russo and Randall Cush

Department of Chemistry & Macromolecular Studies Group, Louisiana State University, Baton Rouge, LA 70803

Tobacco mosaic virus (TMV), a rigid rod with a length of ~300 nm and a diameter of ~18 nm, has been used to probe aqueous solutions containing as matrix polymers either quasi-linear dextran or globular Ficoll dextran. For both architectures, the experiments spanned a wide range of concentrations and macroscopic viscosities. The rates of rotational and translational diffusion of the dilute and weakly depolarizing TMV were measured by depolarized dynamic light scattering. The matrix polymers, which depolarize even less, remained invisible at all concentrations. In addition to comparing globular and quasi-linear polymers, the molar mass of the latter was varied. Absent are the large failures in the Stokes-Einstein relation, which were reported previously by this laboratory for quasi-linear dextran at a single molecular weight (Macromolecules 1997, 30, 4920-4926). Underlying the discrepancy is an improved, if tedious, procedure that excludes not only the depolarized scattering from the optically active polymer matrix but also a residual polarized contribution from the TMV. This weak signal, which arises because of the optical activity of the polymeric matrix, confounds the interpretation when the rotational diffusion coefficient is low. With the improved procedure, depolarized dynamic scattering from rodlike probes can provide rheological information in concentrated solutions of biopolymers. This work was supported by the National Science Foundation--Division of Materials Research.

Tuesday 10:35 Ballroom A MR17

Rheo-optical and rheological behavior in shear of nematic solutions of rodlike polymers

Guy C. Berry and Zhanjie Tan

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Features of the development of defects in the texture of nematic solutions of two rodlike polymers in shear flow are discussed. The rheo-optical behavior ins observed for nematic solutions of poly(1,4-phenylene terephthalamide) reported here and those of poly(1,4-phenylene-2,6-benzobisthiazole) reported elsewhere reveals a systematic similarity, with a sequence of scattering and visual features that develop with time, terminating at a level characteristic of the shear rate developed in steady state. The sequence in steady-state with increasing shear rate reveals sequentially a diffuse scattering with a turbid appearance, diffuse scattering with an opalescent appearance, a broad elliptical scattering along the vorticity with poorly-defined striations, a sharp scattering along the vorticity with well-defined striations along the flow, and a clear, highly birefringent sample, with little scattering. These same features are seen, in the same sequence in time, in transient behavior leading to steady-state. This behavior is attributed to the development of striations with twist distortions alternating in angle relative to the flow, and essentially in the sample plane in the faster steady-state flow. The predominance of the twist distortion in faster flows is attributed to the lower free energy of that distortion in comparison with bend and splay distortions, especially near the planar boundaries of the parallel plates of the rheometer. The deterioration of this texture at slower flows is associated with increasing distortions out of the sample plane, leading to an essentially chaotic spatial distribution of the order tensor at a slow flow, giving a diffuse scattering and rheological behavior somewhat similar to that for a complex fluid comprising particles dispersed in a viscoelastic fluid.

Tuesday 11:00 Ballroom A MR18

Numerical studies of liquid crystalline polymer in simple shear flow

Giorgia Sgalari[1], Harley Klein[1], Jimmy J. Feng[2], Eckart Meiburg[3], and Gary Leal[4]

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Shearing of a pre-aligned liquid-crystalline polymer (LCP) disrupts the natural alignment of these materials and therefore dramatically reduces their high tensile strength. Understanding the interplay between flow history and the spatial distribution of LCP orientation is therefore a crucial step toward optimization of processing conditions and a

full exploitation of the potential of LCPs in structural applications that do not involve fibers. We will review a theoretical, molecularly-based model that we have recently developed, based on the work of Marrucci and collaborators, to describe the rheological behavior of nematic liquid crystals. We will then discuss a relatively novel numerical method that allows us to apply this model to study textural evolution in planar shear flows. Comparisons will be made with available experimental observations.

Tuesday 11:25 Ballroom A MR19

Microscopic and mesoscopic predictions of nematic polymers in shear-dominated flows

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The shear problem for nematic polymers has been advanced through the contributions of Marrucci and his collaborators. This lecture will focus on monodomain orientational dynamics first. We implement a combined mesoscopic-kinetic theory "predictor-corrector" approach to determine which states survive the orientational degeneracy of quiescent nematic polymers in the onset of shear. The phase transitions in the parameter plane of nematic concentration and normalized shear rate separate regions inside of which the multiplicity, steady vs unsteady, in-plane vs out-of-plane, and stability properties are robust. These results complement those of Marrucci, Maffettone, Faraoni, Grosso, Crescitelli, et al. We proceed next to illustrate the role of monodomain attractors as precursors to structure formation in the flow between shearing plates, following results of Rey and collaborators, Kawaguchi et al., and Sgalari et al. Space-time structures are correlated with monodomain attractors and structure scaling properties are discussed.

Symposium FM
Non-Newtonian Fluid Mechanics and Instabilities

Organizers: Satish Kumar and Graham Harrison

Tuesday 9:45 Ballroom B FM15

Effect of shear waves on viscoelastic drop deformation

Kausik Sarkar
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Flow induced drop deformation critically affects the behavior of emulsions. Moreover, single drop dynamics assumes critical importance in microfluidic applications, targeted drug delivery, and microbubble contrast agents for medical imaging. We have been engaged in a computational study of the deformation history of a single drop in imposed time-periodic viscous flows. Previously, we reported a small Reynolds number simulation using front-tracking and finite difference methods that displayed a resonance phenomenon with varying interfacial tension and frequency. In case of a viscoelastic drop with a UCM constitutive relation we found that the drop dynamics changed character significantly, in that the deformation varies non-monotonically with relaxation time. Finally, we found that elasticity generates a system of shear waves that affects the deformation. We will present a perturbative analysis of the wave phenomenon. The effect will be explained with the help of a simple demonstrative example of a layer of viscoelatic fluid underlying another layer of viscous fluid. The importance of the phenomenon in different situations will be investigated.

Tuesday 10:10 Ballroom B FM16

Computing 3-D flows with conformation tensor models

Xueying Xie and Matteo Pasquali
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The conformation tensor is an approximate measure of the micro-structural state of a viscoelastic liquid. This conformation depends on the flow, and in turn modifies the flow by contributing to the total stress. The eigenvalues and eigenvectors of the conformation tensor provide information on the local expectation value of the state of strain

and stress of an ensemble of flowing polymer molecules; thus, conformation tensor models seem to be a good compromise of computational cost and physical accuracy for modelling complex flows.

A few studies have been performed in 3-dimensional flows like planar viscoelastic contraction flow, swirling flow by the finite volume method, and cross-slot flow by the finite element method with the Oldroyd-B and PTT models. So far, fully 3-dimensional computations based on conformation tensor models have not been attempted. Here we apply the DEVSS-G/SUPG Finite Element method to steady viscoelastic flows described by models based on the conformation tensor. Results based on conformation tensor models are obtained in 3-dimensional 4:1 contraction flow and verified by comparison with 2-D results when the channel depth is far larger than the channel width.

The boundary condition on the conformation tensor at open boundaries is an important issue because, in general, the distribution of the conformation tensor there is not known. A general inflow boundary condition based on solving the coupled algebraic equations of fully developed flow at the inflow boundary is proposed to circumvent this difficulty. Calculations show that imposing this boundary condition yields the correct velocity and conformation field in 2-D and 3-D channel flows of Oldroyd-B liquids, for which closed-form expressions of the velocity and conformation components are known.

Tuesday 10:35 Ballroom B FM17

High Deborah number flow modeling with a stable and thermodynamically consistent constitutive equation

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In this work, we first review recent results on mathematical stability of viscoelastic constitutive equations, which implicitly illustrate physical connection of the set of governing equations to thermodynamics. Based on them, in order to solve viscoelastic flow problems we choose the rheological model that are proven globally stable as well as thermodynamically consistent. Also as a test problem, planar 4:1 abrupt contraction flow is considered. Numerical computation employing a finite element method with streamline upwinding demonstrates convergent solution up to Deborah number 120 for the coarse mesh (length of the side of the corner element is 0.1 when the half width of the downstream channel is set to unit), but the numerical scheme ceases to converge for the fine mesh (length of the side of the corner element is 0.01) when the Deborah number exceeds 40. Hence this result also exhibits usual difficulty in mesh convergence such that the numerical degradation in viscoelastic flow computation starts earlier as the discretization mesh becomes finer.

In this study, we suggest an alternative numerical algorithm that dramatically stabilizes the computation procedure and thus increases the limit of achievable Deborah number (at least several times). As a result, we could obtain stable result over 180 of the Deborah number in the case of fine mesh, which within authors' knowledge is the highest value ever computed. The size of the corner vortex exceeds one and half times the half width of the upstream channel. However at this moment, its mathematical validity remains uncertain, and it deserves further investigation in our opinion.

Tuesday 11:00 Ballroom B FM18

Birefringence studies of a shear-thinning polymer solution in a time-dependent axisymmetric stagnation flow

Jason E. Bryant and Wesley R. Burghardt

Department of Chemical Engineering, Northwestern University, Evanston, IL 60208

Axisymmetric flow birefringence is used to interrogate the stress distribution generated by a time-dependent axisymmetric stagnation flow. Fluid in a closed cylinder is forced periodically past a cylindrical obstruction with a hemispherical cap. Fluid elements near the obstruction thus alternately experience uniaxial and equibiaxial extension on a time scale set by the frequency of the oscillatory motion. Polarization modulation birefringence is used to measure integrated shear and normal stress distributions as a function of time and position within the flow. Results may be represented in terms of the time-response of the integrated stresses at particular positions. The spatial dependence of the stress distribution may be compactly presented in terms of spectral coefficients of the time-

dependent stress waveforms determined by Fourier analysis. These data will provide a comprehensive test bed for severe testing of viscoelastic flow simulations.

Tuesday 11:25 Ballroom B FM19

The extensional flow of a wormlike micellar solution past a sedimenting sphere

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

With the use of wormlike micellar solutions as rheological modifiers in many consumer products, the prediction of the behavior of these fluids has grown increasingly important in recent years. Many of the flows experienced by wormlike micellar solutions are complex, containing regions of both shear and strong extensional flows. A complete understanding of the fluid behavior thus requires knowledge of both the shear and extensional rheology of the wormlike micellar solutions. In this talk, we present the results of our experimental investigation into the flow of a wormlike micellar solution past a sedimenting sphere, a prototypical complex flow. The test fluid is a 0.005M CTAB/ 0.005M NaSal solution which is characterized both in shear and transient homogeneous uniaxial extension. A single sphere-to-tube aspect ratio (a/R = 0.0625) is investigated over a wide range of Deborah numbers. As the Deborah number is increased, the drag correction factor, K(a/R, De), is initially found to decrease due to the effects of shear thinning near the sphere walls. At a Deborah number of approximately De = 1.0, the drag correction factor reaches a minimum and begins to increase with increasing Deborah number as a result of the strong extensional flow in the wake of the sphere. At a critical Deborah number, the sedimentation of the sphere becomes unsteady. Flow visualization and particle image velocity (PIV) measurements are used to analyze flow fields for both the steady and unsteady sedimentation of the sphere. An attempt is made to correlate the unsteady behavior of the sphere with the extensional rheology measurements.

Symposium SL
Jamming, Frustration, and Vitrification in Suspensions and Liquids

Organizers: Charles Zukoski and Jennifer Lewis

Tuesday 9:45 Ballroom C SL6

Jamming, clustering and layering in sheared suspensions of platelike particles

Jonathan J. Higdon and Qingjun Meng
Chemical Engineering, University of Illinois, Urbana, IL 61801

Numerical simulations are presented for the rheology of concentrated suspensions of non-Brownian platelike particles. Platelike particles are modeled as rigid planer assembledges of spherical particles. A fast Stokesian dynamics algorithm (with operation count scaling as N ln N) is employed to compute accurate hydrodynamic interactions from dilute systems through high volume fractions. Simulations are conducted for systems with 64 to 512 platelets involving up to 10^4 individual spheres. The suspension rheology and suspension microstructure are documented over a wide range of volume fraction and particle aspect ratio. Details of the suspension microstructure include strong flow induced orientation ordering and formation of large particle clusters. Jamming of the suspension is encountered at a critical volume fraction which is a function of the aspect ratio of the particles.

Tuesday 10:10 Ballroom C SL7

Viscosity bifurcation in pastes

Philippe Coussot[1] and Daniel Bonn[2]
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We show that, when sollicited above a critical stress, typical yield stress fluids (gels, colloidal suspensions, foams, emulsions) start flowing abruptly and subsequently accelerate, leading to avalanches that are remarkably similar to those of granular materials. We demonstrate from rheometrical tests that this is associated to a bifurcation in rheological behavior: for a stress smaller than a critical value, the viscosity increases in time and the material eventually stops flowing. For a slightly larger stress the viscosity decreases continuously in time and the flow

accelerates. Thus the viscosity jumps discontinuously to infinity at the critical stress. In agreement with these observations, MRI-rheometrical experiments under controlled velocity show that these materials cannot flow steadily at a uniform rate smaller than a critical value ($\dot{\gamma}_c$). As a result a "liquid" region (sheared rapidly, i.e. at a rate larger than $\dot{\gamma}_c$) and a "solid" region (static) coexist. The behavior of the fluid in the liquid region follows a simple power-law model while the extent of the solid region increases with the degree of jamming of the material. These results can be qualitatively predicted by a simple theoretical model assuming that the viscosity of the material results from the competition between aging and shear rejuvenation, associated respectively to the organization or disorganisation of the network of particle interactions.

P. Coussot, Q.D. Nguyen, H.T. Huynh, D. Bonn, "Avalanche behavior in yield stress fluids", to appear in Physical Review Letters (April, 2002). P. Coussot, J.S. Raynaud, F. Bertrand, P. Moucheront, J.P. Guilbaud, H.T. Huynh, S. Jarny, and D. Lesueur, "Coexistence of liquid and solid phases in flowing soft-glassy materials", to appear in Physical Review Letters (June, 2002)

Tuesday 10:35 Ballroom C SL8

Local perturbations of jammed colloids

Piotr Habdas and Eric R. Weeks
Physics, Emory University, Atlanta, GA 30322

We used confocal microscopy to directly study the microscopic behavior of colloidal glasses and colloidal supercooled liquids. In particular we embed supermagnetic particles in the system of non-magnetic PMMA colloids and then exert an external magnetic force on these particles to locally perturb the sample in a controlled manner. We investigate the range of these perturbations as a function of magnetic particle size, magnetic force, and colloidal particle concentration, in samples approaching the colloidal glass transition. The results of such studies address broader issues of both a universal description of the origin of the glass transition and also the flow of granular media studied by other groups.

Tuesday 11:00 Ballroom C SL9

Aging effects in rheology and microrheology of colloids

Eugene E. Pashkovski
Technology Center, Colgate-Palmolive Co., Piscataway, NJ 08855-1343

Concentrated colloidal systems such as suspensions, emulsions, gels and pastes often display complex and very intriguing behavior reflecting their metastability and structural disorder. The rheological response of such systems depends on sample' age, similar to molecular and spin glasses. This analogy provides necessary algorithm of studying aging phenomena of "soft" colloidal glasses. We employ the thermodynamic aspect of aging by analyzing the violation of fluctuation-dissipation theorem and combining rheological and diffusing-wave spectroscopy measurements. The fluctuation-dissipation plot obtained for microgel pastes shows that the local and macroscopic dynamic behaviors are strongly disentangled on the time scale comparable with sample age. On the very short time scale, however, no violation is observed. Using thermodynamic approach, we argue that these findings have very general meaning and are system-independent. The thermodynamic approach does not provide us however, with comprehensive insight into structural aspects of aging. Therefore, we discuss some other problems related to characterization of heterogeneous structure of soft glassy materials. In particular, characterization of polysaccharides and microgels using tracer particles with various sizes is described.

Tuesday 11:25 Ballroom C SL10

Rheology and microstructure of depletion flocculated gels

Syed A. Shah and Charles F. Zukoski
Chemical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

The evolution of rheological and microstructural properties of dense colloidal suspensions are investigated as a function of the strength and the range of interparticle attractions. Interparticle attractions are carefully tuned via the addition of non-adsorbing polymer to a suspension of monodisperse octadecyl silica particles in decalin. The strength of the interactions are characterized by measuring the osmotic compressibility of the silica particles in the presence of the polymer and are directly related to the polymer concentration relative to the dilute-semidilute crossover density. Under the influence of short-range attractions these suspensions undergo abrupt phase transitions from a fluid to a non-ergodic gel. This transition occurs over very small changes in the polymer concentration and is monitored via changes in the zero frequency viscosity, the storage and loss moduli and the long time self diffusivity. The scaling of these mechanical properties with polymer concentration is investigated at fixed particle volume fractions and temperature. Changes in the suspension microstructure are also monitored both as a function of the strength and range of interactions from USAXS and USANS measurements that provide direct information about the static structure factor and osmotic compressibility as the phase boundary is traversed. The experimental data is used to critically test liquid state predictions by the microscopic Polymer Reference Interaction Site Model (PRISM) in addition to mode coupling theories that explain the effects of particle caging that lead to changes in the bulk flow properties of suspensions at the gel boundary.

Symposium GL
Rheology of Glasses and Glass-Forming Liquids

Organizers: Gregory McKenna and Alan J. Lesser

Tuesday 9:45 Ballroom D GL1

Dependence of the volume relaxation time on thermal history

Paul Bernazzani and Sindee L. Simon
Chemical Engineering, Texas Tech University, Lubbock, TX 79409

Models of structural recovery, such as the TNM and KAHR models, are known to be inadequate. One of the possible reasons for the shortcomings of these models may be that the assumption that the relaxation time depends only on the instantaneous state of the glass is not valid. In this work, we will report measurements that are aimed at testing this assumption. The evolution of the characteristic relaxation time for volume is measured during volume recovery using a capillary dilatometry and a novel temperature perturbation experiment. Down-jump, up-jump, and memory experiments are performed for a polystyrene. The results suggest that not only does the relaxation time depend on the departure from equilibrium in a way that differs from that commonly assumed, but more importantly, the relaxation time appears to depend on thermal history.

Tuesday 10:10 Ballroom D GL2

Predicting volume relaxation data near glass transition

Grigori Medvedev and James M. Caruthers
Chemical Engineering, Purdue University, West Lafayette, IN 47907

In this paper we attempt to critically assess the ability of various models, proposed to date, to predict the results of the experiments on volume relaxation in glass forming materials in the glass transition region. These experiments include first and foremost the classic set of data obtained by Kovacs for PVAc in the early 60s, where the volumetric response to sudden jumps in temperature was monitored, and also the data by Goldbach and Rehage and, more recently, by Tribone, O'Reilly, and Greener for PS, where the authors studied the volumetric response to sudden jumps in pressure.

When testing a given model against the set of volume relaxation data, it is paramount to make sure that the entire data set is being compared against and not just a few selected thermal histories, which is unfortunately the case in many papers. We have found that the Kovacs experiments involving short annealing times are particularly difficult to predict and the results for them are almost never reported. Successful prediction of the relaxation data in the elevated pressure cases and also in cases of pressure jumps appears to be even more challenging.

As a result of this analysis we report that none of the existing models of structural relaxation is capable of achieving even qualitative agreement with the data. We conclude the paper with a discussion of how the stochastic model of relaxation in glass recently developed in our group overcomes the shortcomings of the traditional models.

Tuesday 10:35 Ballroom D GL3

Evidence of glassy behavior in micellar block polyelectrolytes

Surita R. Bhatia[1], Mark Crichton[1], and Ahmed Mourchid[2]
[1]Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003-9303; [2]UMR 166, CNRS/Rhodia Complex Fluids Laboratory, Cranbury, NJ 08512

We present SANS and rheology for micellar solutions of polystyrene-poly(acrylic acid) block copolymers that can be regarded as attractive colloids. These systems form gels at high effective micellar volume fractions that are suggestive of disordered colloidal glasses. At the gel point, the solution rheology follows the scaling predicted by classical percolation theory, with $G' \sim G'' \sim \omega^{\Delta}$. We argue that this scaling could be due either to formation of a percolated network or a pre-transitional glassy phase.

The addition of cationic and anionic surfactants (DTAB and SDS) can be used to modify the intermicellar interactions and solution rheology. Addition of an anionic surfactant acts to screen attractive interactions and causes a monotonic decrease in the elastic modulus. However, the addition of a cationic surfactant appears to initially induce a stronger intermicellar attraction, leading to gels with a higher elastic modulus. At higher surfactant concentrations, the cationic surfactant begins to screen intermicellar association, leading to a decrease in elasticity.

Tuesday 11:00 Ballroom D GL4

Hygro-thermal effects on the physical aging response of glassy polymers

Yong Zheng and Gregory B. McKenna
Chemical Engineering, Texas Tech University, Lubbock, TX 79409-3121

One cause of long-term dimensional changes in glassy polymers is the gradual evolution of the viscoelastic behavior through aging processes in the glassy state. Many applications of polymers involve changes in relative humidity (RH), under which the materials exhibit aging processes that differ from those in constant RH conditions. In this work, we report results from a study of a glassy epoxy subjected to rapid RH-jumps (isothermal). Similar to the temperature-jump experiments of Kovacs [1], we obtain the volume recovery response in different histories as: intrinsic isopiestics (constant RH), memory effect and the asymmetry of approach. Our results support the hypothesis that water has an effect similar to temperature on structure (volume, enthalpy) of the glass-forming material. However, at the same RH-temperature states, the glasses formed by RH-jumps are different from those formed by temperature jumps. The difference cannot be explained by current theories [2] which simply relate the glass transition temperature to the plasticizer effect. Therefore, the TNM-KAHR model cannot be directly applied for modeling the physical aging response in hygro-thermal histories. Here we describe the similarities and differences between the T-jump and RH-jump results and discuss the implications for structural recovery models that include both temperature and plasticizer effects.

References: [1] A. J. Kovacs, Fortschr. Hochpolym-Forsch. 3, 394, (1964). [2] J. M. Gordon, G. B. Rouse, J. H. Gibbs and W. M. Risen J. Chem. Phys., 66 , 11, 4971-4976, (1977).

Tuesday 11:25 Ballroom D GL5

Long term room temperature aging of polycarbonate resins

Donald G. LeGrand[1], Samuel Miller[2], and Patrick McCloskey[1]
[1]CRD, General Electric, Niskayuna, NY 12307; [2]Plastics, General Electric Company, Pittsfield, MA

Abstract: The notched Izod impact behavior of bisphenol-A polycarbonate samples which had undergone physical aging at room temperature for over 35 years in a laboratory environment has been investigated. The results indicate that materials, which were brittle shortly after injection molding, are still brittle while materials that were ductile are still ductile. These results are in contrast to theoretical predictions based on extrapolation of data obtained on samples, which were aged at temperatures close to the glass transition. These new data suggest that in the absence of environmental effects which include both chemicals and radiation, physical aging of polycarbonates at room temperature is either slower than predicted by extrapolation from higher temperatures or physical aging at room temperature is not altering the ductility. In either event, the effect of physical aging on the ductility of CD's and DVD's should not be of major concern. Tool design, processing conditions, and environmental factors are more critical to the ultimate performance of polycarbonates.

Tuesday Afternoon

Symposium MR

Marrucci Symposium: Molecular Rheology of Concentrated Polymeric Systems

Organizers: Nino Grizzuti and Ronald Larson

Tuesday 1:30 Ballroom A MR20

Interrelations between rheology and defect texture in liquid crystals

Ralph H. Colby
Materials Science and Engineering, Penn State University, University Park, PA 16802

Low stress creep measurements on a thermotropic nematic liquid crystal polymer indicate that it is a viscoelastic solid, with a modulus of 10 Pa and a yield stress of 5 Pa. Both smectics and nematics are viscoelastic solids at very low stress levels, with a modulus that is related to their defect texture. At stress levels somewhat above the yield stress, there is a yielding regime where the deformation rate and defect spacing are power laws in the applied stress. We understand these power laws using the ideas developed long ago by Orowan for the motion of line defects in crystalline solids.

Tuesday 1:55 Ballroom A MR21

Rheology of nanoparticle – linear polymer blends

Tien T. Dao[1], Michael E. Mackay[1], Craig J. Hawker[2], and Brooke van Horn[2]
[1]Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824;
[2]Almaden Research Laboratory, IBM, San Jose, CA 95120

We have blended organic based nanoparticles (ca. 10-30 nm in diameter) with linear polystyrene and found the viscosity is reduced even at 0.5 volume fraction. The nanoparticles were prepared by taking a single polystyrene molecule containing pendant crosslinking groups, collapsing the chain then crosslinking. Thus, every nanoparticle contains a single polymer molecule. The rheological properties of the bulk nanoparticles are interesting and tightly crosslinked particles show a gel-like response with a viscosity greater than the native linear polymer while lightly crosslinked nanoparticles are free flowing and exhibit rheological properties similar to a linear polymer. Upon blending the tightly crosslinked nanoparticles with linear polymer, the viscosity decreases substantially. This effect is certainly caused by changes in the linear polymer conformation although this is yet to be confirmed.

Tuesday 2:20 Ballroom A MR22

Dendritic copolymers: Rheology, molecular structure, and properties of blends with PVC and PS

Norman Wagner[1], Brian Tande[1], and Young Kim[2]
[1]University of Delaware, Newark, DE 19716; [2]DuPont, Wilmington, DE

Polymers with complex architecture, such as hyperbranched polymers and dendrimers have been proposed for numerous applications in drug delivery, nanotechnology, and as rheology modifiers. The numerous end groups can be functionalized to create copolymers. Poly(propylene amine) dendrimers of 4th and 5th generation are end-functionalized to promote compatability with polystyrene and polyvinyl chloride. Measurements of the melt, solution and blend rheology, DSC, small angle neutron scattering and thermodynamic properties are presented and compared with theory and molecular dynamics simulations to elucidate the behavior of this class of copolymer.

Tuesday 2:45 Ballroom A MR23

Dynamics of entangled associating polymers with large aggregates

Alexander N. Semenov[1] and Michael Rubinstein[2]

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We develop a theory for the dynamics in entangled solutions of associating polymers with many stickers per chain. The stickers strongly associate and form large aggregates that control both the equilibrium structure of the system and its dynamics. The association results in formation of micelles that separate macroscopically yielding a reversible gel phase of interconnected closely packed micelles. We identify two mechanisms for stress relaxation: (a) polymer chain diffusion and (b) positional rearrangements of the micelles, and predict that the second process is exponentially slower than chain diffusion. Hence a polymer chain may diffuse through many of its gyration radii during the terminal stress relaxation time. We predict an exponentially strong concentration dependence of the micellar gel viscosity typically involving one or more anomalous regimes where the viscosity is decreasing with concentration. We also show that the chain self-diffusion constant decreases exponentially with concentration in the strongly entangled regime (entangled spacers connecting the stickers).

Symposium SD
Structural Development in Flow

Organizers: Wesley R. Burghardt and R. M. Kannan

Tuesday 3:35 Ballroom A SD1

Experimental observations during early stages of shear-induced crystallization in isotactic polypropylene and poly(1-butene)

Henning H. Winter[1], Aadil Elmoumni[2], and Stefano Acierno[1]

[1]Polymer Science & Engineering and Chemical Engineering, University of Massachusetts, Amherst, MA 01003; [2]Dipartimento di Ingegneria Chimica, Università di Napoli "Federico II", Naples, Italy

Quiescent and shear-enhanced melt crystallization of high-Mw polyolefins was studied by time resolved rheometry, optical microscopy, small-angle light scattering (SALS), birefringence, and turbidity. In quiescent crystallization, spherulites grow of uniform size which suggests simultaneous nucleation and uniform growth rate. The shear effects can be modeled as function of the Weissenberg number, Wi. Shear flow causes (1) an increase in crystallization rate and (2) at sufficiently high Wi, the growth of elongated structures (threads) which are visible in the optical microscope and in anisotropic SALS patterns. The threads thicken until, at later stages, additional spherulites grow. The early growth is attributed to the nucleation of shear induced anisotropic molecular conformations, preferably in the high molecular weight fraction of the iPP sample, while the later growth of spherulites is assumed to occur from the less oriented short chains in the sample.

Tuesday 4:00 Ballroom A SD2

Molecular modeling of flow-induced crystallization of isotactic poly(1-butene)

Pier Luca Maffettone[1], Stefano Acierno[2], Salvatore Coppola[2], and Nino Grizzuti[2]

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The model of Doi and Edwards with the Independent Alignment approximation has proven capable to describe the flow induced enhancement of nucleation rate in semicrystalline polymers. In fact, the evaluation of the free energy change due to macroscopic flow can be used to predict the so-called induction time on the basis of the classical thermodynamics approach. The model is fully predictive as no adjustable parameter is in principle required.

In this work, the induction time is calculated to describe experimental results obtained with a family of isotactic poly (1-butene)s of different molecular weights. Both stationary and transient flow conditions are considered. In spite of some crude simplifying assumptions, a remarkable quantitative agreement between model and experiments is found.

In particular, the model is able to successfully account for the effects of molecular weight on the crystallization kinetics, and provides also a useful framework to evaluate the effects of temperature on flow induced crystallization.

Tuesday 4:25 Ballroom A SD3

Development of a microscopic non-isothermal two phase mixture theory for the description of flow-induced crystallization

Jan Van Meerveld and Markus Hütter
Institute of Polymers, ETH Zürich, Zürich, Zürich CH-8092, Switzerland

A general microscopic non-isothermal two-phase mixture theory consistent with non-equilibrium thermodynamic principles is developed for the description of flow-induced crystallization. Under flowing conditions the nucleation is strongly enhanced in opposition to the growth rate, which need to be considered separately in the model. The crystal morphology after flow-induced crystallization is referred to as the 'shish-kebab structure' with the shish being a long fibril from which lamellae (the kebabs) are growing perpendicularly. The growth dynamics focus on the kebab structure only for reasons of the better theoretical understanding of the lamellar growth dynamics, the experimental accessibility and finally the relevance to the final semi-crystalline material properties, compared to the shish. The thermodynamic driving force for phase change emerges naturally in our thermodynamic analysis containing the contributions of the thermal, mechanical and chemical non-equilibrium state of the system. The latter is affected when the microstructure evolves out of its equilibrium configuration under flowing conditions, described by a reptation model for fast flows. Results are presented considering the classical nucleation theory with the appropriate thermodynamic driving force for start-up of shear and uniaxial elongation flow. Very good agreement is found with the experimentally validated model of Zuidema, Peters & Meijer [Macromol. Theory Simul. 15, 447, 2001], provided the contour path is not stretched into the non-linear regime according to the FENE-P model. However no additional model parameters are introduced in our model besides those associated to quiescent crystallization and non-isothermal rheology. It is observed experimentally that a network is formed during early stages of crystallization, but scaling shows that the nuclei density is far too low to form a network. A refined nucleation scheme is proposed accounting for the embryo formation, which together with the nuclei may be sufficient to form this network.

Tuesday 4:50 Ballroom A SD4

Stratified morphology of a polypropylene/elastomer blend under channel flow

Matthew Moffitt[1], Yahya Rharbi[1], Jiang-Dong Tong[2], M A. Winnik[1], Derek W. Thurman[3], James P. Oberhauser[4], Julia A. Kornfield[3], and Rose Ryntz[5]
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A thermoplastic olefin (TPO) blend consisting of isotactic polypropylene (PP) and a fluorescently labelled ethylene-butene rubber (EBR) impact modifier (25 wt % EBR) was subjected to a short, high-shear pulse within the flow channel of a pressure-driven microextruder. Experiments were performed under isothermal conditions with a known wall shear stress for a specified duration, providing a well-defined thermal and flow history. Immediately following the shear pulse, an increase in birefringence and turbidity was observed in the sample, as has been previously found for semicrystalline homopolymers subjected to intense shear. Ex-situ laser scanning confocal fluorescence microscopy revealed a stratified morphology with well-defined morphology zones that are correlated to different local shear stresses. Closest to the wall, the rubber domains are most highly sheared, forming fibers aligned in the flow direction which are trapped by thread-like crystalline precursors formed during flow. Farther from the wall there is a relatively isotropic layer due to break up of highly elongated drops, followed by another layer with mildly elongated drops, oriented along the extension axis of the shear flow, and an isotropic core at the center.

Symposium FM
Non-Newtonian Fluid Mechanics and Instabilities

Organizers: Satish Kumar and Graham Harrison

Tuesday 1:30 Ballroom B FM20

Rotating flow of viscoelastic fluids in a pipe

Zvi Rusak and John A. Tichy
Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590

The interaction between flow inertia and elasticity in high Reynolds number, axisymmetric, and near-critical swirling flows of an incompressible and viscoelastic fluid in a straight circular pipe is studied. The stresses of the viscoelastic fluid are described by the Oldroyd-B constitutive model (representing the low constant-viscosity Boger fluids). The application of the Oldroyd-B model to streamwise vortices is first investigated and limitations for it are presented. Then, a nonlinear small-disturbance analysis is developed from the governing equations of motion in order to understand the complicated interactions between flow inertia and fluid viscosity and elasticity. The effects of the fluid viscosity, relaxation time, and retardation time on the flow development in the pipe and on the critical swirl for vortex breakdown are explored. It is found that in vortex flows with an axial wake profile, increasing the relaxation time increases the critical swirl whereas increasing the retardation time decreases it. These effects are reversed in vortex flows with an axial jet profile. Also, when the relaxation and retardation times are the same, the critical swirl is the same as that of a Newtonian fluid. The viscoelastic characteristic times also affect the size of the flow perturbation. These results may explain the changes in the appearance of breakdown zones as a function of Reynolds numbers (swirl level) that have been recently observed in the experiments by Stokes et al. (2001) where Boger fluids were used. This work extends for the first time the theory of vortex stability and breakdown to include effects of non-Newtonian fluid.

Tuesday 1:55 Ballroom B FM21

Thermomechanical boundary layers in viscoelastic flow

Thomas Hagen[1] and Jonathan D. Evans[2]
[1]Center of Mathematical Sciences, Munich University of Technology, Munich 80290, Germany;
[2]Department of Mathematical Sciences, University of Bath, Bath, United Kingdom

The objective of this presentation is to give an account of recent advances in non-isothermal channel flows of viscoelastic fluids of Maxwell type (UCM, PTT, Giesekus). In particular, we shall consider the impact of a temperature-dependent viscosity and (single) stress relaxation time on the formation of thermal and mechanical boundary layers in fully developed Poiseuille flow upon entry in a planar channel with heated or cooled walls.

We will show that in strongly viscoelastic flows sudden temperature changes imposed through the channel walls cause physically unacceptable stress singularities for the UCM model. Although similar defects are not to be expected for continuous temperature changes, utmost care is necessary to model such flows appropriately. For flows with a weak dependence on the flow history our study facilitates a direct comparison with analogous results for Newtonian fluids.

Tuesday 2:20 Ballroom B FM22

Development of extrusion instabilities for filled polymers

Dilhan M. Kalyon, Elvan Birinci, and Halil Gevgilili
Highly Filled Materials Institute, Stevens Institute of Technology, Hoboken, NJ 07030

The development of extrusion instabilities is an important and rate-determining industrial problem that is widely studied, especially for the extrusion of linear polymers. Here we will provide extensive data on various material functions and wall slip velocities, and extrusion instabilities for two polymers, which are filled with rigid spherical particles at four volume fractions in the range of 0.1 to 0.4. The data were collected with capillary, slit, and steady torsional flows. The extrusion and wall slip behavior of the two polymers (a high density polyethylene and a poly(dimethyl siloxane) were also characterized to serve as the baseline for the investigation. Overall, the data

suggest the important linkages between the evolution of the wall slip behavior of the suspensions and the extrusion instabilities.

Tuesday 2:45 Ballroom B FM23

Harmonic analysis of rheologically complex fluids

Tom Karis[1], Chul A. Kim[2], and Myung S. Jhon[2]
[1]Research Division, IBM, San Jose, CA 95120; [2]Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

An understanding of molecular rheological properties is vital for manufacturing processes and characterization, especially for microscale processing of thixotropic materials formulations. Although conventional models are available for the investigation of flow with multiphase materials, they appear to neglect the dynamics of the transition, i.e., beyond a "yield" point, the material exhibits a viscous flow behavior. These non-Newtonian flow characteristics are attributed to the interactions of particle clusters with finite cohesive strengths. Here, a novel harmonic analysis based on the discrete amplitude spectrum in large amplitude oscillatory shear (LAOS) is developed to examine thixotropic suspension rheology, and time-dependent structural transition. The LAOS technique is an excellent tool for studying the dynamic nature of wall-slip and non-linear viscoelasticity.

A simple two-segment piecewise constitutive equation, used here for the spectral analysis of non-linear stress waveforms, is an extremely sensitive method for obtaining material functions. We found that only odd harmonics appear in the stress waveform obtained from controlled strain rheometer data. The procedure for calculating the crossover shear rate, the first and second region viscosity, and an apparent yield stress from first and third harmonics are demonstrated. We examined three different materials; channeling grease, commercial solder paste, and a carbon black filled thermoplastic resin used for toner; and we found that the crossover time depends on the shear strain amplitude and the structural transition at the inception of flow. Our analysis provides insight into the molecular level processing control which influences energy dissipation in the application of many complex structured fluids.

Symposium CE
Coating and Extensional Processes

Organizers: Christopher W. Macosko, Robert Secor and Thomas A. Baer

Tuesday 3:35 Ballroom B CE1

Dynamics of chains in high rate elongational flow

Henning H. Kausch and T. Q. Nguyen
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The dynamics of flexible molecular chains is of utmost scientific and technical interest. It influences melt rheology, local chain orientation during processing, diffusion at interfaces and structure and properties of solid polymers. In this presentation model experiments at high rate of flow are reported in which the orientation, uncoiling behavior and rupture of chains has been studied. Two types of flow fields have been investigated: the opposite-jet flow with a stagnation point, and the abrupt contraction flow with open flow-lines. To obtain more detailed information on the degree of segmental orientation, sensitive rheo-optical measurements of retardation have been carried out and a special numerical technique had been devised to compute local birefringence. Differences in orientation behavior of particular sites within a chain (mid-chain, chain ends) have been studied by fluorescence depolarisation of appropriately labeled PS chains. From the thus obtained data it could be concluded that even the center of a long chain changes its spatial orientation with increasing flow rate only gradually and to varying levels of saturation thus contradicting the rapid uncoiling hypothesis.

In conclusion, the affine deformation model is probably one of the simplest representation of chain uncoiling in converging flow. However, coils behave at high rates *in a somewhat rigid manner* allowing for the transfer of intra- and inter-segmental stresses thus explaining extensive chain scission at low *average* segmental orientation.

Tuesday 4:00 Ballroom B CE2

A method of evaluating the extensional elasticity of weakly elastic liquids

David F. James[1] and Nanthan Yogachandran[2]

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A technique has been developed to evaluate elasticity in extension for weakly elastic fluids. The method is similar to that of a filament-stretching rheometer; that is, a fluid sample is initially held by surface tension between two small disks and the disks move apart such that the rate of extension of the fluid is constant. The measured quantity is the distance between the disks when the liquid bridge (or filament) breaks. The breaking length depends on the fluid's viscosity and surface tension and on the rate of extension, and is increased by elasticity. A baseline for zero elasticity was established by testing a variety of Newtonian fluids. Data from these tests showed that the breaking length, scaled by the initial length, is a function only of the capillary number. Tests with known weakly elastic liquids confirmed that elasticity increases the breaking length, i.e., the length for a non-Newtonian fluid was above that for an equivalent Newtonian fluid. The method has been applied to diverse complex liquids such as paints, paper coatings and aqueous drag-reducing fluids. While the method does not yield the measurement of a fluid property, it does evaluate extensional flow resistance of hard-to-characterize liquids, and a patent has been applied for.

Tuesday 4:25 Ballroom B CE3

Transient extensional viscosity of polymer melts in the filament stretching rheometer

Anders Bach[1], Henrik K. Rasmussen[2], and Ole Hassager[1]

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We investigate the transient uni-axial extensional viscosity of polymer melts by means of a filament stretching rheometer. The technique used was developed by Sridhar et.al., but has primarily been used at room temperatures. This limitation in the use of the rheometer may be due to problems regarding a) achieving constant strain-rate, measuring filament diameter inside the oven c) slip between the polymer sample and the rigid end-plate and d) thermosetting of the oven. We control the separation rate of the end plates in order to balance the effect of the no-slip boundary conditions at the end plates. This enables us to achieve a development in cross-section in the middle of the filament for which deviation from ideal uni-axial extension is negligible. Measuring filament diameter inside the oven is solved by using a new laser product on the market. Slip at the end plate is avoided by carefully applying the sample to the end plates, and choosing the melts used in the experiments. The rheometer is constructed as a vertical filament stretching rheometer with an oven built around it. The oven is designed to handle polymer melts in the range from 25°C to 220°C, temperatures being controlled to within ±2°C of the set point. Deviations in temperature are largest at the top of the rheometer where the polymer spends the least time. In the bottom where the sample finds equilibrium before the experiment starts, temperatures are within ±0.5°C of the set point. Experiments were performed on two different polymer melts and compared with experiments done on a Meissner type rheometer.

Tuesday 4:50 Ballroom B CE4

Extensional viscosity of EX rubbers with varying ethylene content

Bhaskar Patham and Krishnamurthy Jayaraman

Chemical Engr & Materials Sci, Michigan State University, East Lansing, MI 48824

The extensional flow characteristics of several elastomers have been characterized by means of skin-core flow through a semi-hyperboloidal die with the elastomer in the core and a low visosity linear polyethylene forming the skin. The Hencky strain in the core is fixed at 4.88 while the strain rates are varied from 1 to 60 s-1. The elastomers are random copolymers of ethylene with propylene, butene and octene and have similar average molecular weights and polydispersity indices. The Trouton ratio curves for the elastomers increase with the ethylene content.

Symposium HS
Heterogeneous Systems: Suspensions, Composite, and Multiphase Materials

Organizers: Daniel De Kee and Yuntao Hu

Tuesday 1:30 Ballroom C HS1

Decomposing dilution, tip stretching and Marangoni effects of surfactants on drop deformation

Y T. Hu
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The dilution, tip stretching, and Marangoni effects of surfactants on the deformation of a drop under flow are decomposed. The dilution effect is calculated using the surface equation of state and change of surface area; the tip-stretching is estimated by analyzing the deformed drop shape; and the Marangoni effect is obtained by subtracting the dilution and tip stretching effects from the total deformation change. For a viscosity ratio of 0.093, the Marangoni effect dominates and its magnitude changes non-monotonically with increase surface copolymer coverage, which leads to a similar non-monotonic change in the overall drop deformation. Tip-stretching is noticeable only at low surface copolymer coverage. For a viscosity ratio of 2.3, the dilution effect dominates and the overall drop deformation is decreased.

Tuesday 1:55 Ballroom C HS2

Numerical simulation of drop breakup and coalescence with soluble surfactant in 3D

Hua Zhou, Vittorio Cristini, John Lowengrub, and Christopher W. Macosko
Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455

In the processing of emulsions and polymer blends, the drop size distributions are determined by two coexisting processes: drop breakup and coalescence. Here we study the effects of surfactants, e.g. block copolymers, on these phenomena and on the shear and normal stress in dilute blends by direct numerical simulation. We use a newly developed 3D adaptive finite-element algorithm. A nonlinear equation of state for the surfactant is used and van der Waals forces are included in the numerical method. Surfactants are transported by convection-diffusion on the drop/matrix interface and between the interface and the bulk phases. Our accurate and robust numerical method features parallel computation and adaptive reconstruction of the finite element meshes describing the bulk phases and the interface.

We find that surfactants affect strongly the breakup and coalescence mechanisms by introducing nonuniformities in surface tension. The related Marangoni (tangential) stresses at the interface greatly inhibit coalescence but in a nontrivial fashion. At small coverages of surfactant at the interface, the critical capillary number for coalescence (below which coalescence will occur) decreases. However, at larger coverages, the critical capillary number reaches a minimum and then increases again and tends to the value for clean (surfactant-free) interfaces. This behavior was first observed experimentally by Leal and coworkers. In this talk, we demonstrate that this behavior is a consequence of a nontrivial evolution of the Marangoni stresses. We also demonstrate that under certain conditions surfactants enhance coalescence by a totally different mechanism. This surfactant induced coalescence occurs when drops are separating and the surfactant-enriched highly-stretched drop tips interact. Finally, we present preliminary results of simulations that indicate that surfactants have a strong effect on the size of the fragments resulting from drop breakup events, and on the total stress in dilute blends.

Tuesday 2:20 Ballroom C HS3

Rheology of immiscible blends with compatibilizer

Sachin Velankar[1], Peter Van Puyvelde[2], Paula Moldenaers[2], and Jan Mewis[2]
[1]Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261; [2]Chemical Engineering, Katholieke Universiteit Leuven, Leuven B3001, Belgium

Block copolymers are routinely employed as surface-active compatibilizers during polymer processing to control the morphology of immiscible polymer blends. The effects of such a block copolymer on the rheological properties of immiscible blends are discussed here. It is shown that flow-induced gradients in interfacial concentration of compatibilizer cause dynamic phenomena that are fundamentally different from those in compatibilizer-free blends.

Model immiscible blends composed of polyisobutylene droplets dispersed in a polydimethylsiloxane matrix were studied in simple shear flow. A diblock copolymer of the same components was used as a surface-active compatibilizer. Experiments demonstrate that the applied flow induces gradients in compatibilizer concentration along the drop surface. The resulting non-uniformities in interfacial tension have several dynamical effects including stabilizing of droplets against hydrodynamically-induced breakup, and stretching of droplet tips in transient flow situations. Gradients in compatibilizer concentration were also found to significantly affect the bulk rheology of blends, e.g. the viscosity and first normal stress displayed by the blends was found to increase with compatibilizer concentration. This represents the first experimental verification of previous numerical simulations that suggest that gradients in compatibilizer concentration confer elasticity upon the blend. The systematic changes in the rheological properties of immiscible blends due to added compatibilizer offer hope that gradient effects may be incorporated into a rheological constitutive equation.

Tuesday 2:45 Ballroom C HS4

Effect of compatibilization on cocontinuity in poly(ethylene oxide)/polystyrene blends

Jeffrey A. Galloway and Christopher W. Macosko
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

Non-equilibrium cocontinuous polymer blends offer an important route to materials with unique combinations of properties not available in a single polymer. Despite numerous applications, blends with a cocontinuous morphology are not well understood. In addition, the presence of a cocontinuous morphology is difficult to confirm experimentally. We have developed several methods to examine the phase continuity of a poly(ethylene oxide)/polystyrene (PEO/PS) system. These include: scanning electron microscopy (SEM) with image analysis, solvent extraction, and rheological measurements. SEM images were analyzed using an algorithm developed at the University of Minnesota. This program was used to quantitatively determine the amount of interface in the samples and thus allowed the most direct evaluation of the phase morphology. The amount of interface in the blends reached local maxima at the boundaries of the region of cocontinuity determined from solvent extraction. Dynamic rheological measurements on the samples showed that the viscosity and elasticity also reached local maxima corresponding to the boundaries of the region of cocontinuity. These methods were used in an investigation of the effect of compatibilization on the region of cocontinuity. Low molecular weight functionalized PEO and PS were used to form block copolymers at the PEO/PS interface during blending. Preliminary results have shown a decrease in the domain size of the blends. An investigation of the effect on the region of cocontinuity is in progress.

Tuesday 3:35 Ballroom C HS5

Flow-induced coalescence in polymeric emulsions

Paula Moldenaers[1], Ellen Van Hemelrijck[1], Peter Van Puyvelde[1], Sachin Velankar[2], and Christopher W. Macosko[3]
[1]Department of Chemical Engineering, Katholieke Universiteit Leuven, Leuven B3001, Belgium; [2]Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261; [3]CEMS, University of Minnesota, Minneapolis, MN

Block copolymers are often used as compatibilizers during polymer processing. For example, the mean droplet size of the dispersed phase of a droplet-matrix type blend is typically reduced due to the addition of block copolymer. One reason for this reduced droplet size is the decrease in interfacial tension due to addition of block copolymer.

However, phenomena such as coalescence suppression and interfacial viscoelasticity due to presence of the diblock on the interface of the droplets may also be important. In this work, the effect of the presence of a PI-PDMS diblock copolymer on the coalescence behaviour of a PI/PDMS blend is investigated systematically by rheology and SEM. Blends with a low amount of copolymer show interfacial viscoelasticity, which gives rise to two different relaxation mechanisms, the droplet relaxation and an interfacial relaxation process. Blends with a high amount of diblock copolymer display coalescence suppression.

Tuesday 4:00 Ballroom C HS6

Normal stresses determination from analysis of drop shape under simple shear flow

Stefano Guido[1], Marino Simeone[1], and Francesco Greco[2]

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Liquid-liquid dispersed systems, such as emulsions or polymer blends, are encountered in a variety of applications, including, e.g., cosmetics design, food processing, and plastics technology. Most studies in this field, both theoretical and experimental, dealt with Newtonian component fluids, and a reasonable understanding of this case has been reached. On the other hand, a comparably clear picture does not emerge from the literature for the case where one or both the emulsion components are non-Newtonian fluids, in spite of its practical relevance. So far, because of the lack of theoretical treatments, the rather sparse experimental results on these systems are of difficult interpretation. As an example, it is not known how the flow-induced morphology of a non-Newtonian liquid-liquid suspension is related to the non-Newtonian properties of the component liquids, such as shear-rate dependent viscosity, and normal stresses (i.e., "elastic" response). In view of this situation, it is apparent that the basic rheological effects associated with non-Newtonian fluid components are best explored in the simplest possible situation, i.e., that of a single droplet in a well-controlled flow field (the "infinite dilution" limit). The shape of a single drop immersed in a flowing immiscible fluid is here determined for slow steady shear, through video-enhanced microscopy and image analysis. The data are interpreted in terms of a novel perturbative solution of the fluidodynamic problem for small drop deformations, where effects of constitutive elasticity of the component fluids are taken into account. By using an elastic matrix fluid and a Newtonian drop, it is found that drop orientation towards the shear direction is directly linked to normal stresses in the matrix fluid. Further results of a systematic investigation of non-Newtonian effects on drop deformation will be also presented.

Tuesday 4:25 Ballroom C HS7

Influence of weak elasticity on droplet behavior for immiscible polymer blends

Wanchai Lerdwijitjarud[1], Ronald G. Larson[2], Anuvat Sirivat[1], and Michael J. Solomon[2]

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The effect of dispersed-phases elasticity on droplet behavior is investigated for blends of polybutadiene in poly(dimethyl siloxane) in a simple shearing flow. The experiment was done in a flow cell mounted on an optical microscope. To study the elasticity effect by itself, the experiments were conducted at fixed viscosity ratios. At the same capillary number (Ca), the steady-state shape deformation of elastic droplets is less than Newtonian droplets and the droplet fluid with the higher degree of droplet elasticity, as measured by the higher value of N1 at high shear rates, deforms less. Correspondingly, the critical capillary number (Ca_{crit}) for droplet breakup increases with increasing elasticity of the dispersed phase. Although weak elasticity of the droplet phase affects the steady-state droplet deformation, in step shear strains under conditions studied, the elasticity of the droplet does not affect the droplet shape, either during the step strain (imposed $Ca > 3Ca_{crit}$; $\gamma = 3$, 6, and 8) or during the relaxation process after the step strain. The steady-state capillary number calculated from the volume-averaged droplet diameter of 20%-dispersed phase blends also increases when the droplet elasticity increases. However, the droplet size at steady state in the 20% blend is smaller than for an isolated droplet of the same dispersed phase and same matrix under identical shearing conditions. This result suggests that, for step-up shear-rate experiment and shear rate between 0.3-2 s^{-1} , the local increases in shear stress present in concentrated blends are more important than coalescence in influencing steady-state droplet size.

Tuesday 4:50 Ballroom C HS8

Stability under shear flow of strings formed in model mixtures of immiscible fluids

Jai A. Pathak and Kalman B. Migler
Polymers Division, NIST, Gaithersburg, MD 20899-8544

We have recently reported* the occurrence of a droplet-string transition in model immiscible emulsions (surfactant-free) composed of polyisobutylene and poly(dimethylsiloxane), when they are sheared under conditions where the gap width between the confining parallel plates approaches the characteristic dimensions of the dispersed droplets. In this work we consider the stability of a long cylindrical domain of a fluid in a phase-separated mixture in a simple shear flow field. Frischknecht** has made elaborate predictions for the stability of an infinitely-long isolated cylindrical domain in a simple shear flow field. These predictions are based on simultaneous solutions of the coupled Cahn-Hilliard and creeping-flow Stokes Equations, from which eigenvalues are derived analytically for long wavelength fluctuations, for different values of the viscosity contrast between the suspended and matrix phase. Using linear stability analysis, she predicts the existence of some critical Capillary number above which the string is predicted to be stable. In addition, she investigates the wavelength dependence of these instabilities. In this work we shall present the results of carefully-designed experiments to test some of these key predictions of the Frischknecht model.

* Migler, K. B. Phys. Rev. Lett. 86, 1023 (2001). ** Frischknecht, A. Phys. Rev. E 58, 3495 (1998).

Symposium GL
Rheology of Glasses and Glass-Forming Liquids

Organizers: Gregory McKenna and Alan J. Lesser

Tuesday 1:30 Ballroom D GL6

Plasticization effects on the viscoelastic behavior of an epoxy resin: Physical aging response after carbon dioxide pressure–jumps

Mataz Alcoutlabi, Francesco Briatico-Vangosa, Lameck Banda, and Gregory B. McKenna
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It is known that if a non-crystallizable polymer is removed from its equilibrium in the liquid state by a sudden decrease in temperature to below the glass transition temperature, it reaches a new glassy, non-equilibrium state. This state has a specific volume and an enthalpy higher than the underlying equilibrium one, so that the volume, under isothermal conditions and in the absence of any external stimulus, decreases over time towards the equilibrium value. This phenomenon is known as structural recovery. Structural recovery effects on other material properties, such as optical or mechanical properties, go under the name of physical aging. It is also well known that small molecules affect the viscoelastic response of polymers by, for example, depressing the glass transition temperature of the material. Therefore, one can anticipate that a rapid change in plasticizer content such as H_2O or CO_2 would result in a change in the volume and viscoelastic response of the material. In this work, we report results from tensile creep tests performed on an epoxy resin in the presence of carbon dioxide at different pressures (P_{CO2}) and at a constant temperature below the glass transition temperature T_g. Time - P_{CO2} superposition was applied to the data to account for the plasticization effects. In addition, physical aging of the epoxy films was investigated using sequential creep tests after carbon dioxide pressure down-jumps at constant temperature and also after temperature down-jumps at constant carbon dioxide pressure. The isothermal pressure down-jump experiments showed physical aging responses similar to the isobaric temperature down-jump experiments. However, the aging rate for the CO_2-jump was slightly lower than that for the T-jump and the retardation time for the P_{CO2}-jump experiments was up to 6.3 times longer than the T-jump conditions. These unanticipated differences will be discussed in terms of energy landscape ideas.

Tuesday 1:55 Ballroom D GL7

Cooperative motion in glass-forming liquids

Brian M. Erwin and Ralph H. Colby

Materials Science and Engineering, Penn State University, University Park, PA 16802

Evidence for a length scale for cooperatively rearranging regions in glass-forming liquids from NMR experiments, diffusion experiments and computer simulations is summarized. Armed with the temperature dependence of the distribution of cooperatively rearranging regions and their fractal dimension (from simulations) allows the construction of a simple scaling model for glass formation. The rheological consequences of this model are discussed in detail, including a prediction of the activation energy in the glassy state from rheology measurements above the glass transition temperature.

Tuesday 2:20 Ballroom D GL8

Thermally stimulated recovery of inelastic deformation in epoxy/amine crosslinked and uncrosslinked systems

Hiroshi Kawakami[1], Hiroshi Yamanaka[2], and Yukuo Nanzai[1]

[1]Department of Mechanical and Physical Engineering, Graduate School of Osaka City University, Osaka, Osaka 558-8585, Japan; [2]Department of Mechanical Engineering, Graduate School of Osaka City University, Osaka, Osaka 558-8585, Japan

Recovery of inelastic deformation in glassy epoxy resins was studied by means of thermally stimulated deformation recovery (TSDR) and differential scanning calorimetry (DSC) measurements. Two types of samples were prepared from bisphenol-A type epoxide monomer: one was a crosslinked structure cured by 4, 4'-diaminodiphenylmethane and the other was a linear uncrosslinked structure polymerized by aniline. The samples were deformed in compression first in the rubbery state and subsequently compressed further in the glassy state. After deformed in the glassy state, the samples were subjected to TSDR and DSC measurements. The TSDR results indicated that, for the crosslinked samples, the magnitude of inelastic strain recovering at temperatures below the glass transition point Tg was larger than that of the uncrosslinked samples. However, the DSC results indicated that the strain energy released from the crosslinked samples at temperature below Tg was less than that from the uncrosslinked samples. From the TSDR and DSC results, we evaluated strain energy density which was defined as the amount of released strain energy divided by unit recovering strain at temperatures below Tg. The value of the strain energy density for the crosslinked samples was much less than that of the uncrosslinked samples. Such result indicates that, for the crosslinked epoxy resin deformed in the glassy state, glass-like strain recovers quite cooperatively with rubber-like strain at temperatures below Tg in contrast to the glass-like strain recovery in the uncrosslinked resin.

Tuesday 2:45 Ballroom D GL9

Structure-property evaluation of controlled epoxy networks

Nikhil E. Verghese[1], Maurice J. Marks[2], and Ha Q. Pham[2]

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Epoxy thermoset resins are used in a variety of applications ranging from adhesives, coatings and printed circuit boards all the way to structural composites. It is well known that one of the most important parameters controlling properties is network structure. Several methods exist to change the network structure namely, composition and molecular mass of the epoxy pre-polymer, functionality and type of curing agent, stoichiometric ratio and processing conditions such as cure times and temperatures. This vast number of options however poses a problem in finding consistent data sets in the literature to build a database that can be used for performance model development.

In an effort to understand and eventually correlate and predict the effects of molecular network structure on the thermal and mechanical properties of thermoset polymers, a study was launched to synthesize and characterize a model system based oncross-linkable epoxy thermoplastics (CETs). These CETs were made using bisphenol A diglycidyl ether as the epoxy, bisphenol A or tetrabromobisphenol A as extender, and sulfanilamide as curing agent to give thermosets with uniquely controlled network architecture. Results will be shared that describe the effects of network architecture on various thermal, thermo-mechanical and mechanical properties.

Tuesday 3:35 Ballroom D GL10

A model for predicting the super-Arrhenian behavior of glass forming materials

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A fundamental understanding the origins of the non-Arrhenian (i.e. WLF) dependence of relaxation time on temperature for glassy materials remains an important unanswered question. Recent experiments and molecular simulations show that glassy materials are dynamically heterogeneous in the vicinity of Tg, at a length scale of 3-10nm. Moreover, experiments on thin films and nanopore glass also indicate that glassy behavior is observed for systems with similar characteristic lengths. Given the near universality of WLF behavior for glassy materials, we postulate that the essential physics emerges at the nanometer scale. We have developed a mesoscale model that exhibits super-Arrhenian dependence of relaxation time on temperature. We model matter as a set of continuum elements at the nanometer length scale. The elements are elastic and interact via the standard conservation laws. Each element can be in one of several states, where each state is characterized by a reference shape, elastic moduli, and specific heat. The elastic energy of the system is calculated by FEA. The total energy (elastic+internal) is used in Monte Carlo type updates to observe the relaxation of the autocorrelation function of the system. We believe that the prediction of super-Arrhenian behavior for this system is significant, since the model did not assume super-Arrhenian behavior instead only employed elastic elements that interact by the traditional conservation laws. Because the individual elements can have different moduli and specific heats, the energy landscape is a function of temperature. We show how the changes in the landscape cause the super-Arrhenian behavior exhibited by our model. This idea is fundamentally different from the usual picture of a fixed energy landscape. The evolution of the energy landscape with temperature results because the individual elements have an internal energy and well as an elastic component, which we believe will be an inherent feature of any mesoscopic rescaling of a glass forming material.

Tuesday 4:00 Ballroom D GL11

Studies of nano and molecular scale reinforcement on the yield and fracture behavior of glassy polymers

Alan J. Lesser
Polymer Science & Engineering, University of Massachusetts, Amherst, MA 01072

Currently a number of studies have focused on reinforcing glassy polymers using structures of nano or molecular scale. The primary engineering property being modified by these reinforcements includes the solid-state modulus of the glass. However, relatively little attention is given to how these reinforcements affect other engineering properties such as yield and fracture of the modified glass. In this paper, we discuss the effects that one class of nano-scale reinforcement (namely organically modified nanosilicates) as well as one class of molecular reinforcement (anti-plasticizers) have on the yield and fracture behavior of polymer glasses. With regard to nanosilicates we discuss both intercalated and exfoliated morphologies and present new approaches of synthesizing highly filled nanosilicates (> 20% wt.). We discuss the role of particle-particle interaction on the nonlinear yield response. With regard to molecular scale reinforcements, we probe the efficiency of molecular fortifiers with regard to their structure and size relative to the size of a glassy network.

Tuesday 4:25 Ballroom D GL12

Dependence of mechanical properties and viscoelastic relaxation on nanoclay loading of intercalated polycarbonate nanocomposites

Alex J. Hsieh and Paul Moy
Weapons and Materials Research Directorate, U.S. Army Research Laboratory, APG, MD 21005-5069

The effect of nanoclay loading on the mechanical behavior and viscoelastic relaxation response of intercalated polycarbonate (PC) nanocomposites is investigated. Incorporation of nanoclay significantly affects the extent of tensile elongation; change of failure mode from ductile to brittle deformation occurs at clay loading of about 3 wt.%. These PC nanocomposites nevertheless exhibit elastic-plastic deformation upon the compressive loading, and their apparent yield stress, regardless of the clay content, is slightly higher than that of the pure PC. Thermal degradation evidenced by a decrease in the glass transition temperature appears to be dominant in the mechanical response, particularly near or above the percolation threshold of nanoclay.

The dependence of apparent yield stress upon the clay content as well as upon the strain-rate of the compression testing will be correlated with the corresponding viscoelastic relaxation response obtained for these PC nanocomposites.

Tuesday 4:50 Ballroom D GL13

Study on nonlinear deformation mechanism in glassy epoxy resin by birefringence technique

Tomita Masatoshi, Kawakami Hiroshi, and Nanzai Yukuo

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Nonlinear deformation mechanism in crosslinked glassy epoxy resin was studied by means of birefringence technique. Epoxy samples were deformed in constant-rate tension up to nonlinear ranges at various temperatures. During the deformation, tensile stress(σ) and birefringence(Δn) were simultaneously measured. Application of modified stress-optical rule (MSOR) to σ and Δn enabled us to separate the stress σ into glassy component (σ_G) and rubbery component (σ_R). Changes of the stresses σ_G and σ_R with strain were compared with those for linear polymers. The stress σ_R increased almost linearly with strain. This result was similar to those in linear polymers. The stress σ_G increased with strain up to the maximum value at the yield point. Passing the maximum point, σ_G in the epoxy resin decreased and then turned to increase with strain, while the stress σ_G in linear polymers leveled off or decreased. Such results indicate for the epoxy resin that glassy strain (strain component contributing to the increase in σ_G) increases cooperatively with rubbery strain (strain component contributing to the increase in σ_R) even after the yield point.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 University Ballroom PL3

Rheophysics of wormlike micelles

Jean-François Berret
CNRS-Rhodia Complex Fluids Laboratory, Cranbury, NJ 08512

Wormlike micelles result from the self-assembly of surfactant molecules into locally cylindrical aggregates. In this talk, I will present an overview of the rheology of wormlike micellar solutions. Three main features of the flow properties of wormlike micelles will be addressed : the shear-thickening transition observed at very low concentration, the shear-banding instability found in the semidilute viscoelastic solutions, and the tumbling and flow-aligning behaviors of the nematic state. Results obtained using transient rheology, flow birefringence, small-angle neutron scattering and nuclear magnetic resonance under shear will be shown and discussed.

Symposium SD
Structural Development in Flow

Organizers: Wesley R. Burghardt and R. M. Kannan

Wednesday 9:45 Ballroom A SD5

Structure development is shear flow using a diffuse interface model

Patrick D. Anderson, Bert Keestra, and Han E. Meijer
Eindhoven University of Technology, Eindhoven, The Netherlands

A numerical model, based on a Galerkin spectral element technique, is applied to study morphology development and the kinetics of phase separation in a homogeneous shear flow. The theory of Cahn and Hilliard, describing the free energy of a non-uniform system with local and non-local gradient terms, is used in the frame work of non-classical thermodynamics described by de Groot and Mazur. A complete set of equations is derived which governs both phase separation and hydrodynamical effects as breakup and coalescence. Dependent on the shear rate and the Capillary number different morphologies are found. To validate the simulations of the structure development, the results of the diffuse interface modeling are compared with results from light scattering experiments (SALS) on the well-known polymer blend system of PMMA and SAN. Moreover, rheological properties of the different blends are discussed.

Wednesday 10:10 Ballroom A SD6

Dispersion visualisation in high viscosity ratio molten polymer systems under time and temperature-dependent shearing flow

Frej Mighri and Michel A. Huneault
Polymer Materials Engineering, Industrial Materials Institute, National Research Council, Boucherville, Quebec J4B 6Y4, Canada

Previous work on dispersion visualization in viscoelastic systems has generally been done at room temperature using low viscosity model fluids deformed at low deformation rates. In this investigation, a specially designed transparent

Couette-flow Cell has been used to visualize the deformation and breakup of single molten polymer drops in high viscosity ratio polymeric systems at shear rates up to 50 s^{-1} (steady state and time-dependent) and temperatures up to 230°C. The deformation and breakup mechanisms observed for polymer-polymer systems was different from those obtained with Newtonian systems. First, at high deformation rates, the normal forces cause the dispersed droplet to contract in the flow direction and to expend in the vorticity direction (i.e., perpendicular to the flow direction). The breakup occurs during flow due to flow disturbance that causes the ends of highly elongated particles to get in slightly different planes. Secondly, the polymer droplet can be dispersed by an erosion mechanism, a breakup mechanism never observed in Newtonian systems. It is suggested that in molten polymer systems, typically several orders of magnitude more viscous than Newtonian model fluids, the stresses at the interface can out weight the particle cohesive forces resulting in surface erosion. These phenomena were observed in systems of moderate interfacial tension (polyethylene/polystyrene), of low interfacial tension (ethylene-propylene copolymer in polypropylene) and without interfacial tension (high viscosity PDMS in low viscosity PDMS).

Wednesday 10:35 Ballroom A SD7

Neutron scattering from melts in complex flows

T. C. B. McLeish[1], Lian Hutchins[2], R Richards[2], Julian Bent[2], Tim Gough[3], Phil Coates[3], Tim Nicholson[1], Alexei Likhtman[1], and Richard Graham[1]

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The deformation of chains in complex flows has been directly measured by SANS, and compared to model molecular calculations along streamlines of the flow, in a large collaboration of chemistry, physics and applied mathematics. Convective Constraint Release is a vital physical ingredient determining molecular deformation.

Wednesday 11:00 Ballroom A SD8

Measuring interfacial tension by retraction of surfactant-laden drops: Numerical simulation and experiments

Sachin Velankar[1], Hua Zhou[2], Hyun-Kyoung Jeon[2], and Christopher W. Macosko[2]

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The imbedded fiber retraction method (IFRM) and the deformed drop retraction method (DDRM) are well-established procedures for measuring the interfacial tension between immiscible homopolymer melts. We employ computational fluid mechanical simulations to investigate whether these methods yield the correct values of the equilibrium interfacial tension when a surfactant is present on the interface between immiscible fluids. This is of direct relevance to numerous practical situations in which block copolymers are employed as surfactants to reduce the interfacial tension between immiscible homopolymers.

An initially spherical drop is deformed into a short fiber by shear flow of the suspending matrix, and then allowed to retract back to spherical shape due to interfacial tension. The local interfacial tension on the drop surface is assumed to decrease as the local concentration of surfactant increases. Drop shapes are obtained by solving the Stokes flow equation using an adaptive finite-element algorithm. It is found that the applied flow field couples with the local surfactant concentration to induce a gradient in interfacial tension on the surface of the drop. The resulting Marangoni stress and gradient in the local capillary pressure are found to affect the retraction process significantly. The chief result is that depending on the initial concentration of surfactant, the retraction of the drop is significantly slower or faster than expected from its equilibrium interfacial tension. Accordingly, analyzing the data using the DDRM or the IFRM yields values of interfacial tension that are significantly different from the equilibrium value. Most interestingly, presence of surfactant causes a new relaxation process that can be related to very slow relaxation of concentration gradients of the surfactant. The simulations are compared to retraction of compatibilized polyethylene drops in a polystyrene matrix.

Wednesday 11:25 Ballroom A SD9

Flow-induced structure formation in drag reducing polymers

Matthew Liberatore, Anthony J. McHugh, and Emily Pollauf
Chemical Engineering, University of Illinois, Urbana, IL 61801

High molecular weight aqueous polymer systems provide large drag reductions in turbulent flow at relatively small concentrations. A vast library of literature spanning decades lacks strong physical understanding of these polymers under both laminar and turbulent flows. An investigation of several drag reducing systems is investigated under shear flow. Aqueous solutions of hydrolyzed polyacrylamide, polyacrylamide, and polyethylene oxide with two to five million average molecular weight have been examined within a concentration regime of 100 to 4000 parts per million by weight. Experimental protocols include: standard rheological characterization, rheo-optical characterization, optical microscopy, and chromatography analyses. Rheo-optical response of high molecular weight aqueous polymers readily demonstrates varying degrees of flow-induced structure formation and shear thickening under flow. A couette device capable of shear rates up to 8000s-1 provides dynamic and steady state viscosity, transmittance, birefringence and dichroism data via modulated polarimetry. Results suggest the size of flow-induced structures that form under shear flow range from clusters of entangled chains to almost completely phase-separated droplets. The kinetics of formation and relaxation vary with shear rate and polymer. Upon cessation of flow, most solutions demonstrate complete reversibility to a homogeneous state on relatively short time scales. In addition, some results suggest phase-separation under shear while other solutions completely phase-separate days after being sheared. Correlations with on-going drag reduction studies demonstrate that such structure formation plays an important role in the drag reduction process.

Symposium CE
Coating and Extensional Processes

Organizers: Christopher W. Macosko, Robert Secor and Thomas A. Baer

Wednesday 9:45 Ballroom B CE5

Relating the jetting behavior of model polymer solutions to their extensional flow properties

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Solutions used in ink-jet printing typically contain dissolved polymers whose molecular weight and concentration are such that they behave as constant viscosity elastic liquids. Differences in fluid viscoelasticity show up very clearly in the jetting behavior of these liquids; however, the elasticity level is too low to be measured with the help of either dynamic mechanical experiments or the first normal stress difference in shear. In the present work an innovative extensional viscometer, in which fluid extensional stresses are inferred from the measurement of changes in flow rate through a vertical capillary (Agarwal and Gupta, 2002), was used to measure the apparent Trouton ratio of several polystyrene-in-decalin solutions. These liquids, along with Newtonian mineral oils of comparable viscosity, were also examined for their jetting behavior using a commercially available jet head; drop sizes were determined using high-speed sequence photography. As expected, it was found that increasing viscoelasticity by increasing the polymer concentration or polymer molecular weight resulted in an increase in the Trouton ratio. This increase revealed itself in the ease of separation of the liquid from the jet head and in the presence or absence of satellite drops.

S. Agarwal and R.K. Gupta, An innovative extensional viscometer for low-viscosity and low-elasticity liquids, *Rheol. Acta*, 2002 (in press).

Wednesday 10:10 Ballroom B CE6

Drop formation dynamics of constant low viscosity, elastic fluids

Viyada Tirtaatmadja[1], Justin J. Cooper-White[1], Gareth H. McKinley[2], and David V. Boger[1]
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The dynamics of drop formation from a nozzle under gravity have been investigated as a function of elasticity using a set of low viscosity ideal elastic fluids based on polyethylene oxide (PEO). All solutions had the same shear viscosity, equilibrium surface tension, and density, but differed greatly in elasticity. The minimum drop radius in the early stages of drop formation (necking) was found to confirm potential flow theory within this region, independent of the solution used, with the necking dynamics being controlled by a delicate balance between purely viscous, inertial and capillary forces. Elastic effects are only observed upon the formation of the pinch region, after which there is a large variation in the drop development to break-off observed between the various elastic solutions. The initial dimensions of these pinch points, and the times at which they form for each fluid, are shown to be a function of the Zimm relaxation time, and interestingly, the concentration of the polymer, even though all of these solutions are well within the dilute regime. The break-off lengths and times to breakup of the thread produced between the primary drop and the nozzle increase with increasing elasticity of the solutions. The experimental observations can be accurately described by a one-dimensional theory that correctly incorporates inertial, capillary and elastic effects in the falling thread. The critical pinch time observed experimentally corresponds to the rapid transition from an inertio-capillary balance to a regime in which the polymer elasticity balances the capillary pressure. The finite extensibility of the flexible PEO chains limits the extent of the latter regime and controls the length of the filament formed before droplet breakup occurs. The effective relaxation times calculated from these experiments indicate that although the solutions are nominally dilute near equilibrium (i.e. $c^* < 1$), in the extended state there are significant inter-chain interactions.

Wednesday 10:35 Ballroom B CE7

Coating the outside of a rotating cylinder with non-Newtonian fluids

Jacqueline Ashmore[1], Amy Q. Shen[1], Gareth H. McKinley[2], and Howard A. Stone[1]
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One type of fluid flow common in industrial processes involves the deposition of a thin film on a moving substrate. The mathematical description of the free surface shape in such coating problems involves a nonlinear third-order differential equation. In the early 1940s, Landau, Levich and Derjaguin used matched asymptotics to solve the equation and determine the thickness of the uniform film which coats a plate or cylindrical fiber when it is withdrawn from a bath of Newtonian fluid sufficiently rapidly. Since then, matched asymptotics have been used to derive theoretical descriptions of the film thickness for Newtonian and non-Newtonian fluids in a variety of geometries. A comparison between theoretical and experimental results for the thickness of an axially uniform film coating the outside of a rotating cylinder which is partially submerged in a bath of non-Newtonian fluid will be presented for a number of different constitutive models. Our results build on and extend those already in the literature (for example Gutfinger and Tallmadge, 1965; Spiers, Subbaraman and Wilkinson, 1975; de Ryck and Quere, 1998). The importance of geometry in characterizing film thickness will be described, and some issues concerning stability will be discussed.

Wednesday 11:00 Ballroom B CE8

Viscoelastic roll coating flows

Mitchell A. Johnson and Douglas W. Bousfield
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In roll-to-roll processing of liquids, a small amount of dissolved polymer can have a large impact on the performance of the system. The extreme nature of the rolling nip environment creates a wide range of non-Newtonian behavior for industrially significant coating liquids. Viscoelasticity has its most apparent effect on the stability of application and metering processes, dramatically reducing the maximum speed at which a uniform film can be applied to the web.

Experimental and computer-aided finite element investigations of roll coating flows with purely viscous, elastic, and viscoelastic liquids reveal the effects of shear-thinning viscosity and fluid elasticity on the flow rate, gap width, and pressure profile. Measurements of gap width and film thickness indicate a correlation between increased flow rate and fluid elasticity, for a given linear load, in forward mode operation. Finite element simulations with Oldroyd-B and multi-mode Giesekus model fluids reveal larger roll separating forces for a corresponding gap and flow rate.

Wednesday 11:25 Ballroom B CE9

Viscoelastic film splitting flows

Gladys Zevallos[1], Marcio S. Carvalho[1], and Matteo Pasquali[2]

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Many industrial processes involve film-splitting between two rotating rolls. Except at low speeds, the flow is three-dimensional and results in more or less regular stripes in the machine direction. This instability can limit the speed of the process if a smooth film is required as a final product. In the case of Newtonian liquids, the stability of the film-split flow is determined by the competition of capillary forces and viscous forces near the free surface. Non-Newtonian behavior can drastically change the nature of the flow near the free surface; when minute amounts of flexible polymer are present, the onset of the three-dimensional instability occurs at much lower speeds than in the Newtonian case. At high enough Capillary number, ribs can grow to form filaments that eventually break to form small droplets. In this work, the two-dimensional, viscoelastic flow near the free surface is analyzed by solving with the Finite Element method the momentum and continuity equations coupled with differential constitutive models (Oldroyd-B and FENE-P). The results show how the liquid properties affect the stress field and reveal a new elastic mechanism that may explain the early onset of the three-dimensional instability when viscoelastic liquids are used.

Symposium HS
Heterogeneous Systems: Suspensions, Composite, and Multiphase Materials

Organizers: Daniel De Kee and Yuntao Hu

Wednesday 9:45 Ballroom C HS9

Steady state shear flow and relaxation in concentrated immiscible polymer blends

Jan Mewis, T. Jansseune, and Paula Moldenaers

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The stresses in flowing immiscible blends can be divided in a contribution from the bulk phases and one from the interface. A relaxation technique is used to separate these contributions in model blends of nearly Newtonian components. Both shear stresses and the first normal stress differences are considered. The interfacial contribution is related to the surface area and the orientation of the interface between the two phases and hence it can be related to the phase morphology of the blend. The orientation of the dispersed phase is estimated from the ratio between normal and shear stresses. The rheological behaviour of some, but not all, rather dilute blends can be described quite accurately with available models. No clear indication of phase inversion can de detected in the system under investigation. This seems to be related to the presence of fibrillar structures in concentrated blends in stationary conditions at higher shear rates. The results for the component stress from the bulk phases differ substantially from those for the interfacial contribution. They can, however, be understood on the basis of the same structural picture. Again the position of phase inversion is not clear. Also the relaxation of the shear stress and of the first normal stress difference is considered over the full concentration region. The relaxation-concentration curve can show two maxima, consistent with some literature data for other rheological parameters. Possible explanations are discussed.

Wednesday 10:10 Ballroom C HS10

Morphology-diffusion coupling in multiphase mixtures

Ali El Afif[1], Daniel De Kee[2], Ricardo Cortez[1], and Donald P. Gaver III[3]
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Mass transfer into structured media generally exhibits behavior that cannot be correctly described by Fick's laws. This is attributed mainly to the individual and non-linear character of the microstructure that brings about inertia and viscoelasticity into the process. Here, we investigate diffusion processes into immiscible fluids characterized by complex deformable interfaces. In case of mixtures consisting of Newtonian immiscible fluids, the internal structure stems mainly from the presence of an interface separating the different components. The presence of such a physical discontinuity necessitates other variables to track the internal morphological deformations. Here, we adopt the Doi-Ohta mesoscopic approach which characterizes the interface by two structural variables: a scalar denoting the interfacial area density and a traceless second order tensor accounting for the shape anisotropy. The governing equations of this newly derived model clearly show the effects of the coupling arising between the interface deformation and diffusion. Mass transfer becomes non-Fickian and in turn the diffusion fluxes modify the size and shape of the interface.

Wednesday 10:35 Ballroom C HS11

Finite element analysis of drop deformation in the viscoelastic two-phase entrance flow described by the Leonov model

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The finite element numerical scheme was developed to analyze the deformation of a droplet in the converging viscoelastic two-phase flow. In the present study a viscoelastic droplet suspended in a viscoelastic medium was mainly considered, where the Leonov model was chosen as a constitutive equation for physically consistent and mathematically stable description of fluid elasticity. We used quadratic triangular elements for velocity as well as extra-stress components, whereas linear interpolation was applied for strain rate tensor. The penalty function method was also employed in order to eliminate the pressure variable from the system of equations. At the interface between the droplet and suspending medium, the normal and shear stress balances must hold with interfacial tension taken into account. When we apply the penalty function method, the balance condition appears as terms of the forcing vector in the set of discrete equations, and thus the final element matrix equation becomes free from the pressure term. Using unstructured mesh generator combined with auto-remeshing techniques, we could describe the shape of a highly deformed droplet in the flow field. Then the results for viscoelastic two-phase flow were compared with those computed for purely viscous flow in order to clearly demonstrate the role of fluid elasticity. In addition, we extensively investigated the effect of variation of operational and material parameters such as flow rate, relative drop size, viscosity ratio, interfacial tension and relaxation times for each phase on the droplet deformation mechanism.

Wednesday 11:00 Ballroom C HS12

Interfacial tension in an immiscible blend containing a thermotropic liquid-crystalline polymer

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In this study, we investigated the measurement of interfacial tension between two immiscible polymers in a blend containing a liquid crystalline polymer and poly(dimethyl siloxane) (PDMS) using a simple extension of the thread break-up method as developed by Zhou et al [1] and Son et al [2]. We selected an LCP (PSHQ6,12) featuring an accessible nematic-isotropic transition for direct investigation of nematic ordering effects. Following the break-up of LCP fibers in a matrix of the flexible PDMS, the formed ellipsoidal-shaped LCP droplets retract to the equilibrium spherical shape at a rate controlled by an orientationally-averaged interfacial tension and the rheological properties of both the LCP and PDMS. By measuring the shape evolution of the LCP droplet, we can estimate the average

interfacial tension assuming rheological simplicity (Newtonian behavior) for both polymers. By examining the late stage of thread break-up we have determine the interfacial tension for a range of temperatures bracketing the nematic-isotropic transition revealing values from 0.25 to 3.0 mN/m. On crossing the transition from a nematic to isotropic phase of the LCP, the interfacial tension features a stepwise increase similar to the steady shear viscosity of the LCP. We have also used real-time retardance and orientation imaging with a CRI LC-Polscope to observe the birefringence and orientation evolution during the break-up of the LCP fiber and retraction of the deformed ellipsoidal drop. With such data, we are attempting to determine the role of molecular orientation at the LCP surface in determining interfacial tension.

[1] J. Non-Newtonian Fluid Mech. 2000, v91, 221. [2] Polymer, 2000, v42, 7209.

Wednesday 11:25 Ballroom C HS13

The shear modulus of random polydisperse soap foam

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Dry soap foams consist of polyhedral gas bubbles separated by thin liquid films, which can be modeled as minimal surfaces under static conditions. The Surface Evolver is used to calculate the microstructure and shear modulus of random foams with cell-size distributions ranging from monodisperse to highly polydisperse (individual bubble volumes vary by two orders of magnitude). Simulations indicate that the shear modulus G and surface energy E both decrease with increasing polydispersity; in fact, $G/E = 0.155$. Ad hoc models for the shear modulus by Derjaguin and Stamenovic predict larger values for the constant: 4/15 and 1/6, respectively. The results for the shear modulus are in excellent agreement with experimental data for monodisperse and slightly polydisperse foams and highly concentrated liquid-liquid emulsions. We have also found a very simple relationship between surface energy and mean bubble radius: E is proportional to R. Consequently, the shear modulus can be accurately predicted from the surface tension and bubble size distribution of a dry foam.

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

Symposium VP
Viscoelasticity of Polymer Liquids

Organizers: Jay Schieber and Shi-Qing Wang

Wednesday 9:45 Ballroom D VP1

Brownian dynamics simulations for dilute polydisperse polymers in good solvents including effects of chain scission

Chih-Chen Hsieh and Ronald G. Larson
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Despite recent success using Brownian dynamics (BD) simulations to describe flows of dilute polymer solutions in theta solvents, applying BD simulations to more general cases such as polydisperse polymers in good solvents is limited by the huge computational load, especially for complex flows. In order to overcome this difficulty, we propose using a molecular-weight-dependent effective Kuhn length to compensate the good solvent effects, and also introduce "stress-averaged" molecular weight and "smart-binning" sampling schemes to describe polydisperse polymers. To describe good-solvent effects, the effective Kuhn length is determined by matching the simulated coil size of the polymer at the equilibrium state to that of the real polymer. This method gives us a similar stress-strain curve in extensional flow as we obtain using a more rigorous bead-bead repulsion method to incorporate excluded volume. The "stress-averaged" molecular weight is a representative molecular weight calculated based on the stress contribution of each molecule to the plateau extensional viscosity, which gives more accurate predictions of the whole start-up curve that does the simple weight-average molecular weight. "Smart-binning", on the other hand, is a

parsimonious representation of the molecular-weight distribution in the BD ensemble of chains that weights most heavily those polymer components that contribute the most stress. These schemes have been tested in simple extensional, simple shear, relaxation, and turbulent flows. By comparing the simulation results averaged over millions of runs, BD simulations combined with proposed methods prove able to produce accurate results with only several hundred chain realizations. This not only gives a huge saving in computation resources but also makes BD simulations applicable to more general, commercial dilute polymer solutions. The effects of polymer chain scission in strong flows will also be simulated and the results will be compared with experimental data of poly(ethylene oxide) in water.

Wednesday 10:10 Ballroom D VP2

Brownian dynamics simulation of symmetric and asymmetric three-arm branched polymers in dilute solution

Yong Min Lee and Yong L. Joo
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853

Much of the research on constitutive modeling and simulation of branched polymers to date has focused on concentrated solution and melt systems. It has been known that the dynamical behavior of branched polymers can significantly be different from linear polymers even in dilute solutions. The goal of this study is to understand detailed configuration and stretch of branched polymers in dilute solutions under various flows. In particular, we are interested in stress response and conformational hysteresis of branched polymers in complex flows. Using input from stochastic simulations of multi-bead spring models, we wish to develop a simple model for the underlying microstructure of branched polymers in a dilute solution. The new model will ultimately be used in complex flow simulation of branched polymers in dilute solutions such as turbulent drag reduction. We first examine dynamics of asymmetric, three-arm branched polymers in a dilute solution. Each arm of branched polymers is modeled as either FENE dumbbell or FENE springs in the stochastic simulation. Predictions with asymmetric branched polymers are compared those with symmetric branched and linear polymers. The effects of arm length and internal modes of each arm on dynamics including relaxation behavior and transient responses in shear, elongational and mixed flows are addressed.

Wednesday 10:35 Ballroom D VP3

Recent Stressmeter developments

Arthur S. Lodge
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The Lodge Stressmeter is a slit die rheometer which yields values for shear rate, shear stress, and the first normal stress difference (calculated from transverse slot hole pressure data) in steady shear flow. Previous models have had shear rate ranges up to 3,000,000 reciprocal seconds and shear stress ranges above 100 kPa at temperatures up to 200C. As a preliminary investigation of the feasibility of using a Stressmeter as an on-line sensor for monitoring commercial pilot plant solution polymerization reactions, the pressure-difference-measuring transducer system has recently been successfully tested at ambient pressures up to 2000 psi. With the aim of measuring low-viscosity liquids (such as aqueous polysaccharide solutions) at very low shear rates for possible applications to oil well cracking projects, another Stressmeter model has recently been developed with the aim of reaching shear stress values below 0.1 Pa. Newtonian liquid hole pressure data for transverse slots have been compared with values computed by Jackson & Finlayson.

Wednesday 11:00 Ballroom D VP4

Standard reference materials: Non-Newtonian fluids for rheological measurements

Carl R. Schultheisz[1], Kathleen M. Flynn[2], Stefan D. Leigh[2], and Gregory B. McKenna[3]
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The National Institute of Standards and Technology (NIST) develops Standard Reference Materials for calibration, quality assurance and for research into improved measurements. Two fluids that demonstrate shear thinning and normal stresses typical of polymeric fluids have been developed as standards for rheological measurements. SRM

2490 is a solution of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane. SRM 2491 is a polydimethylsiloxane melt, with less temperature dependence than SRM 2490. NIST certifies the shear-rate dependence of the viscosity and first normal stress difference at 0 °C, 25 °C and 50 °C, and the linear viscoelastic behavior from dynamic mechanical measurements over the same temperature range.

Wednesday 11:25 Ballroom D VP5

Viscoelastic effects in elongational flow: A new orifice impedance method

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[1]Vilastic Scientific, Inc., Austin, TX 78716; [2]University of Texas at Austin, Austin, TX 78712

A method is described for determining both the extensional viscosity and extensional elasticity of thin non-Newtonian fluids by measuring the impedance to oscillatory flow in an orifice constriction. The impedance components, resistance and reactance, are resolved from measurements of the magnitude and phase of the pressure across and the flow through the orifice. In order to obtain the extensional impedance, the orifice impedance is decomposed into extensional, shear and kinetic energy components. The apportionment of these components is illustrated for Newtonian water and a non-Newtonian polyethylene oxide solution. Additional examples such as polymers with various degrees of flexibility are presented. The extensional impedance is used to calculate the extensional viscosity, elasticity, relaxation time and viscoelastic Trouton ratios.

Wednesday Afternoon

Symposium SD
Structural Development in Flow

Organizers: Wesley R. Burghardt and R. M. Kannan

Wednesday 1:30 Ballroom A SD10

Small angle neutron scattering (SANS) study of shearing effects on drag reducing surfactant solutions

Yunying Qi[1], Kenneth Littrell[2], Pappannan Thiyagarajan[2], Yeshayahu Talmon[3], Zhiqing Lin[1], and Jacques L. Zakin[1]

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Dilute drag reducing surfactant solutions are very sensitive to shear. Similar to the effects of temperature, counterion/surfactant chemical structure and counterion/surfactant concentration ratio, shear can induce microstructure transitions which affect drag reduction effectiveness and rheological properties (shear viscosity; apparent extensional viscosity; first normal stress differences). In this paper, the effects of shear on three types of drag reducing surfactant solutions, Arquad 16-50/NaSal (5mM/5mM) (viscoelastic, high apparent extensional/shear viscosity ratio), Arquad S-50/NaSal (5mM/12.5mM) (non-viscoelastic, high apparent extensional/shear viscosity ratio), and Arquad 16-50/3,4-CH_3-Benzoate (5mM/5mM) (viscoelastic, low apparent extensional/shear viscosity ratio) are studied by small angle neutron scattering (SANS) experiments together with their rheological properties, drag reduction abilities and microstructures. The differences in the rheological behavior and the SANS data of the solutions are explained by the different responses of the microstructures to shear.

Wednesday 1:55 Ballroom A SD11

Degradation and recovery of drag-reducing surfactant solutions

Kazimir Gasljevic, Klaus Hoyer, and Eric F. Matthys

Mechanical and Environmental Engineering, University of California, Santa Barbara, CA 93106

We have worked for some years on the implementation of drag-reducing solutions in industrial systems. One of the essential components of the proposed technology was our development of a successful heat transfer control strategy that allows us to recover full heat transfer in heat exchangers thanks to intentional local micellar degradation. As an aspect of this work, we have investigated the intentional temporary degradation and subsequent recovery of the drag-reducing properties of some surfactant solutions. The temporary degradation was achieved by exposing the fluid to mechanical stresses and temperature jumps. The recovery time, defined in this case as the time needed by the surfactant system to return to its undegraded drag reduction level, can vary from seconds to minutes or more, depending on the surfactant concentration, counterion concentration if any, and temperature. The results generally show a linear increase of the drag reduction level with time, with the relationship being essentially independent of the flow velocity and the initial level of degradation. The recovery after cessation of flow is different from the recovery under turbulent flow conditions.

Wednesday 2:20 Ballroom A SD12

Nano particle formation in turbulent impinging jets

Brian K. Johnson and Robert K. Prud'homme

Chemical Engineering, Princeton University, Princeton, NJ 08544

The rapid precipitation of insoluble drug compounds in turbulent jet reactors can be used to form nanometer-sized particles that aid in the bioavailabilty of many drug formulations. To successfully form the nano particles and to prevent aggregation or uncontrolled growth a block copolymer stabilizer must be incorporated into the impinging jet streams. The control of the time scale of self-assembly of the block copolymer relative to the time scale of the particle crystallization is crucial for successful particle formation. The time scale of the crystallization is controlled by the details of turbulent micromixing in the jet, which we measure using competitive reactions.

Wednesday 2:45 Ballroom A SD13

Rheology of polypropylene nanoclay composites

Girish S. Galgali[1], Ashish K. Lele[1], Malcolm R. Mackley[2], and Ramesh Chellaswamy[1]

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Melt-processibility and several product performance issues of polymer-layered-silicate (PLS-) nanocomposites are dictated by the dispersion of the clay tactoids. The microstructure of the nanocomposites influences it's flow behaviour and is itself influenced by flow.

Rheological properties of Polypropylene-clay nanocomposites were studied under shear flow and near quiescent conditions. The nanocomposite hybrids were prepared by melt intercalation in the presence or absence of a compatibilizer. For compatibilized hybrids the linear rheological data such as creep and low amplitude frequency sweep response suggests that above 5 wt% clay loading, the clay tactoids form a percolating network, which offers significant resistance to shear deformation. For instance, the zero-shear viscosity of compatibilized hybrids was found to be three to four orders of magnitude higher than that of the uncompatibilized hybrid or the matrix polymer. Further, the creep data showed an interesting time evolution that is indicative of subtle microstructural changes. Non-linear rheological data obtained from stress-ramp experiments showed apparent yield behaviour above a critical stress. The rheological data indirectly indicates orientation of clay tactoids at higher stresses. A rheo-XRD technique was used for in-situ measurement of the flow-induced orientation during processing of these materials. At high shear rates, Herman orientation functions close to 0.9 were observed, which suggest significant orientational order. Relaxation of orientation on cessation of shear was also reported. The orientation relaxation time matched the rheologically measured relaxation time, which suggests that above a critical shear rate range the clay tactoids have insufficient time to relax their orientation thereby causing a the observed yielding.

Wednesday 3:35 Ballroom A SD14

In situ SAXS studies of shear-induced orientation in model polymer/clay nanocomposites

Laura M. Dykes[1], Wesley R. Burghardt[1], and Ramanan Krishnamoorti[2]

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We report studies of the structural dynamics in model polymer/clay inorganic nanocomposites. Various organically modified clays are dispersed in relatively low viscosity poly(dimethyl siloxane), leading to rheologically complex materials that may be conveniently studied at room temperature. We utilize an annular cone and plate x-ray shear cell, in conjunction with synchrotron x-ray scattering to enable real-time measurements of the average degree and direction of platelet orientation within the flow-gradient (1-2) plane in shear flow. We characterize orientation in steady unidirectional shear flow, upon flow reversal and cessation, and during large-amplitude oscillatory shear. Average platelet orientation increases modestly with increasing shear rate, while the average platelet orientation moves somewhat closer to the flow direction. In all samples studied, orientation does not relax significantly upon cessation of shear.

Wednesday 4:00 Ballroom A SD15

Preliminary investigation on configuration space distribution function in concentrated suspensions

Jing Fan[1], Alan L. Graham[1], Lorne A. Davis[2], and Francis A. Gadala-Maria[3]

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Even the simplest model systems such as suspensions of neutrally buoyant spheres in Newtonian liquids exhibit a rich variety of non-Newtonian behavior such as normal stresses and shear-thinning of the viscosity at high solids loading. There is a growing body of experimental, numerical and theoretical work that links the origin of this non-Newtonian behavior to flow-induced asymmetries in the pair-distribution function of particles. The objective of this work is to determine the microstructural origin by measuring the evolution of the configuration space distribution function of these non-Newtonian phenomena in initially well-mixed model suspensions of mono-dispersed particles in shear flows under conditions such that only hydrodynamic forces exert an appreciable effect.

The suspensions of neutrally buoyant, mono-dispersed polymethyl methacrylate spheres in a viscous Newtonian fluid with the volume concentration of 50% solids were placed in a wide-gap Couette and subjected to flow. The evolution of the three-dimensional positions of individual particles in an initially well-mixed suspension in shear flow (wide-gap, annular Couette flow) was obtained by reassembling multiple thin sequential nuclear magnetic resonance image slices, each of thickness 0.5 mm. The probability of finding a particle at a given location relative to a reference particle (configuration space distribution function) was determined as a function of strain. The results are compared to that of a computer simulation assuming a random distribution of 2000 particles.

Wednesday 4:25 Ballroom A SD16

The rheology of dispersions under high electric fields, compressive and shear flows

Frank E. Filisko[1] and Yongang Meng[2]

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The rheology of dispersions has taken on an additional dimension with the recognition that imposed E/M fields could drastically change the properties, i.e. electrorheological and magnetorheological materials. Understanding of this behavior remains unsatisfactory from both a theoretical and mechanistic viewpoint. Although E/M field induced aggregation of particles is no doubt related to the behavior and is material dependent, the yield stress values are virtually independent of the materials, around 3-5 kPa or less. Recent studies of ER / MR active dispersions under compression and tension (vs. shear) record much higher values for the corresponding yields, 50 - 200 kPa. Additionally, many studies show that ER fluids in the preyield or solid state have shear modulii the MPa range. Additionally exposing certain dispersions to E/M and shear fields aggregates particles rapidly to form lamellar structures (walls vs. columns) oriented in the shear direction. These structures require a much greater force to shear which is transmitted from the electrodes to the particulate surfaces by a frictional mechanism. A current model ER/MR fluids involving these observations proposes that these frictional forces are inadequate to shear the particulate structures and the main mechanism for flow is by slippage between the electrodes and the adjacent particle lamellae. Thus the limiting feature of the strength of ER fluids is not the shear strength of the lamellae but the frictional force between the electrodes and the lamellar surfaces. A method to test this hypothesis is to increase the frictional force between the electrode surface and the particle lamellar surface. This is accomplished by moving the electrodes together and monitoring the normal force and shear stress vs. voltage. The results are quite remarkable and involve not only a Bingham model but also concepts of granular flow to explain them. These results will be presented in this paper.

Wednesday 4:50 Ballroom A SD17

Estimation of the pumpability of concretes from the mortar phase rheology

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The transport of the fresh concrete by pumping is an important process and widely used in the actual concrete technology. Developments of the pumping equipment and new findings in mineral and chemical admixtures in last decades obliged the concrete technologists to undertake more sophisticated researches on pumping concretes.

The improved workability, durability and strength of the pumping concretes owe these qualities to the invention of super plasticizers, also known as high range water reducers. Pumping concretes are fluid but also have sufficient cohesion provided by fine particles as stone powder or fly ashes. The workability of the pumping concrete is actually determining by standard workability tests such as slump, slump-spread and K-slump tests. For the workability of the pumping concrete which needs more complex properties the classic slump test is inadequate. We may explain these complex properties by using rheological constants of the mortar. It is evident that slump test can not give sufficient information about these specific properties. The rheological constants (yield value and plastic viscosity) of the mortar can be determined with a co-axial viscosimeter. Rheological tests on mortars were carried on with a Mettler RM 180 Rheomat co-axial viscosimeter. The mortars were placed in viscosimeter tube following 8, 18 and 28 minutes from the beginning of their mixing with water. A program of 8 steps was performed and the $\gamma-\tau$ diagrams were drawn. All the mortars showed a thixotropic behavior conformable to Bingham model. The linear regression on the linear parts of these graphics gave the yield value and the plastic viscosity of the mortars.

It is convenient to summarize the conclusions of this research in three different rubrics: modifications occurred in the rheological behavior of the mortar phase, changes observed on the properties of the concretes and the influences of the rheological constants of the mortar on the concrete pumpabilities

Wednesday 5:15 Ballroom A SD18

Curing process monitoring by rheology

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A method was developed to track viscosities during curing. Viscosity was studied and tracked for the curing process of silicone and acrylic. Curing commonly happens in the final stage of the coating while drying or other plastic process. Curing always enhances the water resistance of the aqueous coating or the product durability over its lifetime. Heating followed by an isothermal holding process was designed to account for effects of both temperature and time on the curing process. Data was fitted into an equation. Rate of the viscosity increase versus temperature is calculated according to the equation. Time for 100-fold viscosity increase is calculated. Results will be used to direct and control the curing process.

Symposium CE
Coating and Extensional Processes

Organizers: Christopher W. Macosko, Robert Secor and Thomas A. Baer

Wednesday 1:30 Ballroom B CE10

Low flow limit on slot coating of viscoelastic liquids

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Slot coating is a common method in the manufacture of a wide variety of products. The thickness of the coated liquid layer is set by the flow rate fed to the coating die and the speed of the substrate, and is independent of other process variables. An important operating limit of slot coating is the minimum thickness that can be coated at a given substrate speed, generally referred to as the low-flow limit. For Newtonian liquids, the mechanism that defines this limit balances the viscous, capillary and inertial forces in the flow. Although most of the liquids coated industrially are polymeric solutions and dispersions that are not Newtonian, most of the previous analyses of operability limits in slot coating dealt only with Newtonian liquids. In the case of liquids made non-Newtonian by polymer viscoelasticity, stresses can alter the force balance in various parts of the coating bead and consequently the onset of instability. In this paper, the low-flow limit in cases of non-Newtonian liquids is examined by both theory and experiment. The Oldroyd-B and Giesekus constitutive equations that approximate viscoelastic behavior of polymer solutions were used, together with momentum and continuity equations, to model two-dimensional flow in the downstream part of a slot coating bead. The equation system was solved with the Finite Element Method. The results show how the viscoelastic properties can affect the stress field in the liquid and the force balance near and at the downstream meniscus, thereby illustrating how non-Newtonian behavior can alter the flow instabilities that determine the coating window of slot coating. The flows themselves were visualized by video microscopy and the low-flow limit was found by observing, at given substrate speed, the feed rate at which the flow becomes unstable. Different solutions of low molecular weight polyethylene glycol and high molecular weight polyethylene oxide in water were used in order to evaluate the effect of mildly viscoelastic behavior on the process.

Wednesday 1:55 Ballroom B CE11

Detachment of the polymer from the rolls in shear roll mill

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The shear roll extrusion or continuous shear roll milling process is a continuous processing method, that involves two grooved rolls, which are counter-rotating without being enclosed in a stationary barrel. The process allows the carrying-out of various unit operations associated with the commonly employed extrusion processes including melting, pressurization, homogenization, dispersion and pelletizing. The material needs to adhere to only one of the two rolls. For adequate processing a detailed understanding of the adhesion and detachment of the material being processed to and from the heated rolls is essential. In this study the processing of a simple high density polyethylene melt is investigated using thermal imaging cameras, industrial scale equipment and 1-D mathematical modeling of the process. The wall slip and rheological behavior of the polyethylene (various material functions in shear as well as the uniaxial extensional stress growth function) are also characterized in detail. At the point of detachment from the rolls the shearing stress is in the same range as the critical shear stress at which the no-slip condition fails in simple shear flows of the same polyethylene melt. Ramifications of the findings on the selection of operating conditions and geometry will be elucidated.

Wednesday 2:20 Ballroom B CE12

Calendering of poro-elasto-viscoplastic sheet and coating

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Calendering is the name of a forming process in the polymer industry, of a finishing operation in papermaking, and of a post-coating smoothing step. Common to all three is squeezing flow of a solid-like material between two counter-rotating rolls. The fundamentals are the deformation mechanics of porous, elastic, viscoplastic material.

A constitutive framework based on the thermodynamics with internal variables, the concept of stress-free state and the poro-viscoplastic flow rule was developed to model the nonlinear mechanical behavior of complex poro-elasto-viscoplastic materials. Finite compressible elastic (Blatz-Ko) model was used to describe deformations at low stress regions in the calendering nip. A yield surface, based on Drucker-Prager yield criterion, separates these elastic regimes from the post-yield finite compressible viscoelastic response. The governing equations of mass, momentum were solved with the Galerkin / Finite Element Method. The computational mesh deformed like a finite elastic solid. Most of the densification is attained upstream of the nip. The greater the Coulomb's friction coefficient at the web-roll contact surface, the higher the porosity reduction. Both front and back tensions lower the compressive stress and the porosity change in the nip.

These computer-aided results were challenged by experimental visualization and measurement of the permanent microstructural changes of paper fiber networks. Porous handsheets of Aspen Pulp, labeled with a fluorescent dye

(BASF's Basonyl Red 560), were calendered in a soft-nip lab calender under different speeds and loads. Two-photon confocal microscopy and image processing (deconvolution, correction for depth-wise intensity drop, and segmentation) provided visualization and estimates of the permanent porosity and surface roughness change of the fiber network. Both porosity and surface roughness drop with higher loading and lower speeds.

Wednesday 2:45 Ballroom B CE13

A pressure drop/flow rate relationship for flows of extensional-thickening liquids through porous media

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Flows through porous media are characterized by essentially extensional kinematics. When the flowing fluid is viscoelastic, if its extensional viscosity increases with the extension rate, then the pressure drop may be governed by the extensional-thickening behavior. In this case, the classic Darcy's law does not represent accurately the dependence of pressure drop on the flow rate. In this work, a relationship between the pressure gradient and the seepage velocity is presented that carries information about the liquid behavior on extension. First of all, a pressure drop/flow rate relationship for an ideal pore channel is obtained. Then a capillaric model theory is applied to obtain the sought-for relationship. Comparisons with experimental data available in literature were performed for validation purposes. Experimental data for a Boger fluid flowing in a model porous medium were also obtained, and were compared with the predictions of the proposed relationship. The comparisons revealed that the proposed relationship has good prediction capabilities in a representative range of flow rate.

Wednesday 3:35 Ballroom B CE14

Stress development and crack formation in colloidal thick films during drying

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Here we use the two-phase fluid model with the compressive yield stress constitutive equation to describe stress development in drying films of aggregated colloidal slurries. Our approach considers colloidal films of arbitrary thickness for which we estimate the elastic properties using measurements of the compressive yield stress and shear yield stress for these films. Applying this approach to drying films offers an opportunity to further test the validity of the compressive yield stress constitutive equation and allows us to examine directly the changes in the elastic properties of the films as a function of the colloidal interaction forces in the system and therefore to probe the role that these forces play in stress evolution during drying. We are able to accurately predict curvatures that we calculate from experimentally measured substrate deflection using our estimates of the elastic modulus from the compressive yield stress constitutive equation allowing us to calculate average stresses and strains in the films directly from measured deflection. Our observation of the stress profile in these drying films shows that there are three main stages in cases where no cracks occur in the film during drying. The three stages are; an initial saturated phase where the body is undergoing consolidation and the stresses match the compressive yield stress in the film; a second phase when consolidation stops and a near linear stress decay is observed in the film that matches the rate of mass transfer from the drying film and a third stage when the stress in the film undergoes a second increase to a final plateau residual stress. In cases where cracks occur beyond the peak stress we limit our analysis to the stress evolution in the saturated phase. We identify conditions in the films that are likely to result in the formation of cracks and link these conditions to interaction forces.

Wednesday 4:00 Ballroom B CE15

Modeling of dry spinning of polymer fibers

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Dry spinning is an important fiber spinning process used in cases where the polymer may be susceptible to thermal degradation or where certain surface characteristics of the filaments are desired. Despite its commercial importance however, dry spinning has received very little attention in the literature in recent years, particularly with regard to modeling studies. In this study, a comparison is made of the predictions of quasi-two-dimensional mathematical model simulations of dry spinning based on Newtonian and viscoelastic constitutive equations for the spin dope. The viscoelastic model is based upon a modified Giesekus constitutive equation with a temperature and composition dependent relaxation time. The simulation algorithm includes the effects of the glass transition on the expected solution viscosity and relaxation time behavior along the spin line. Predictions of axial velocity, tensile stress and composition profiles for the two cases, suggest the role of viscoelasticity in the locking-in behavior associated with fiber solidification along the spin line. The radial variations of the composition and temperature profiles predict the skin-core morphology of the fiber and its relation to the formation of crenulated structures in the as-spun fibers is investigated. The effects of model parameters and processing conditions are also discussed.

Wednesday 4:25 Ballroom B CE16

Numerical simulations of the effect of local material property variation on deformation of webs during loading

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This research of this research is to develop models for the handling of polymeric webs that will lead to processing free from material defects and with a minimum machine downtime and product loss. The approach is to model existing and proposed web transport processes using first principles mechanics. A novel feature of the work is the characterization and simulation of spatial variations in web properties. Numerical models incorporating simulated spatial variations may then be used to investigate interactions between the multiple mechanisms that cause material defects and product loss during web transport.

Here we report on the effect of non-uniform density distribution on the deformation and failure of non-woven webs. The web considered in this study is a thermally bonded network of polymeric fibers. The web was scanned optically and the resultant gray-scale distribution was used to infer local density. The spatial distribution of density was analyzed statistically and statistically equivalent "simulated webs" were generated for use in finite element simulation of web transport. Results indicate that spatial heterogeneity strongly influences both the general web behavior and the tendency for the web to produce instabilities that lead to manufacturing defects such as folds and wrinkles.

Wednesday 4:50 Ballroom B CE17

The design of profile extrusion dies using 3-D computational fluid dynamics

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ABSTRACT Efficient fully three-dimensional, non-Newtonian flow algorithms have been available for several years to aid in the design of flat dies used to extrude polymers. However, there are few tools available, which can be used in a practical way by an engineer tasked with designing a complex profile die in a reasonable period of time. This paper demonstrates through actual examples how the efficient use of 3-D CFD algorithms and automatic finite element mesh generators can be used to eliminate much of the "cut and try" from profile die design. The effect of die swell on the profile shape downstream of the die exit is also examined can be compensated for in the die design.

Wednesday 5:15 Ballroom B CE18

Rheological behaviour and model of alumina-polymer-based composites

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In the paper, new approach to development of composite bearing like alumina-aluminum-polymer-steel substrate has been revealed. The requirements to the rheological model have been formulated to develop adequate model describing tight-strained state of the composite. We suggested the following requirements to be used in rheological model of the composite: 1. Since the composite include hard alumina layer and steel substrate that exhibit plasticity, the irreversible deformations has to be considered as plastic in nature. Deformations develop only after excess of some critical yield strength for the particular layer of the composite. 2. if the deformations are smaller then yield strength, the deformations at constant stress have to grow up step-by-step to final value; 3. Cyclic loading increases summarized plastic deformation of the composite; 4. Curve of deformation vs. time at constant load exhibits a linear dependence in one of plotted region. 5. At unloading the retardation of deformations (elastic return) has to be

observed; 6.Stress at constant deformations is relaxed. The composite of hard alumina-aluminum can be presented as elastic-tenacious-plastic rheological model of the composite. Structural equations of the integral model of the composite looks like (H || N || St-V) - (H-N || H). Rheological equation depends on a level and form of stress applied on model. The polymer can be presented as rheological model consisting from the Maxwells' model and elastic element. The composite exhibits linear relation of stress curve, whereas unloaded composite shows retardation of deformations (elastic return) shown as downfall segment of the curve. The relations of experimental data and calculated data revealed close agreement of developed rheological model and real mechanical behavior of the composite. The above stated conditions are found to be used in investigations of mechanical and rheological properties of the alumina-aluminum-polymer-steel composite systems.

Symposium HS
Heterogeneous Systems: Suspensions, Composite, and Multiphase Materials

Organizers: Daniel De Kee and Yuntao Hu

Wednesday 1:30 Ballroom C HS14

Polypropylene nanocomposites

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Polypropylene (PP) is widely used for many applications due to its low cost, low density, high thermal stability and resistance to corrosion. Blending polypropylene with clays to form nanocomposites is a way to increase its utility by improving its mechanical properties. Compared to conventional composites, polymer layered-silicate (PLS) nanocomposites have maximized polymer-clay interactions since the clay is dispersed on a nanometer scale. This results in lighter materials with higher modulus and strength making them desirable for some applications such as exterior automobile parts.

Polypropylene nanocomposites are still challenging due to the lack of affinity of organophilic PP for hydrophilic clay. The goal of this research is to prepare PP nanocomposites by direct melt-blending of polypropylene with silicate/surfactant and organosilicate/surfactant lamellar mesostructures which have been synthesized.

TEM and x-ray diffraction are commonly used to characterize nanocomposites. However these two complementary techniques present several drawbacks. On the other hand, rheology in the molten state is an alternative way of monitoring the degree of exfoliation of the clay : the dispersion of the clay into the polymer matrix results in a higher modulus especially at low frequency. This solid-like behavior is related to the formation of a clay network inside the polymer matrix. We attempt to derive a quantitative model.

Wednesday 1:55 Ballroom C HS15

Effect of shear deformation and temperature on the crystallization morphology of intercalated polypropylene nanocomposites

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Polymer/clay hybrid materials, which have been prepared with significantly enhanced solid-state mechanical, dimensional, permeability, and flame-retardant properties relative to the pure polymer, have motivated interest in a number of technological applications. It has been hypothesized that processing variables such as shear rate, shear strain and temperature affect end-use material properties by their influence on the morphology produced during crystallization. Therefore, we investigate the effect of these variables on the crystallization of polypropylene/intercalated organophilic montmorillonite composites by means of time-resolved small-angle light scattering. We report experiments conducted under both quiescent and shear flow conditions. Invariant measures of density and orientation fluctuations are used to measure characteristic crystallization times. The effect of shear deformation on nanocomposite scattering is investigated in particular. We quantify the different ways in which flow affects polymer crystallization in the neat and in the intercalated hybrid materials.

Wednesday 2:20 Ballroom C HS16

Exfoliation, networking and yield behavior in nano-suspension of modified montmorillonite clay

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Commercial organically-modified montmorillonite clay is dispersed in organic solvents to elucidate the state of full exfoliation. The nano-suspensions show yield behavior at weight fractions as low as 1 %, achieving a significant yield stress level of several hundred Pa at a few wt. %. These nano-suspensions are studied with Bohlin-CVOR in terms of the plateau modulus from oscillatory shear, steady-state compliance and yield stress from creep and creep recovery as a function of the loading level. The stress-induced sol-gel transition at the point of yield is indeed impressive, with the apparent steady-shear viscosity dropping eight decades. The rheological measurements reveal that due to efficient exfoliation, which is verified by X-ray diffraction measurements, and to extremely high surface area of the silicate plates a percolating structure is established at a small fractional percentage of the particle volume fraction. Steady shear observations are also made using ARES to further illustrate the rheological behavior of these nano-suspensions.

Wednesday 2:45 Ballroom C HS17

Rheological properties, processing and morphology of polymer-layered silicate nanocomposites

Hojun Lee and Gareth H. McKinley
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The steady-state and linear viscoelastic rheological properties of polymer-layered silicate nanocomposites were investigated. The materials, based on a commercial nylon melt, a PMMA melt, and a dilute polystyrene solution, were prepared by dispersion of an alkyl ammonium modified montmorillonite over a range of clay concentrations, and were melt-processed via a lab-scale twin-screw extruder. X-ray diffraction and TEM showed that the nanocomposites have an intercalated morphological structure, with an increase of the gallery-spacing of the clay layers compared to that of the pure clay. Measurements reveal that the complex moduli of these nanocomposites are strongly dependent on the clay content and the resulting mesoscopic structure of nanoclay particle within the matrix. As the clay loading increases to about 4-6%, a plateau modulus at low frequencies is observed, indicating a solid-like rheological response due to the percolated nanoclay structure in the nanocomposites. The linear viscoelastic response of these percolated nanocomposites follows an intermediate behavior between a chemically cross-linked structure and an entangled system. Indeed, the relaxation time associated with the percolated nanoclay structure is found to be on the order of 103 seconds depending on the matrix materials, whereas the dynamics of the polymer chains calculated by the Rouse model are unchanged with respect to the clay incorporation. Superimposed steady-shear/oscillatory measurements were performed to investigate the effects of the background shear field on the complex modulus. Results show that the storage moduli of the nanocomposites quickly decrease while shearing, and slowly recover following the cessation of shear. Fourier analysis of TEM images shows the shear-induced orientation of plate particles along the flow direction. WAXD analysis of the melt-processed composites allows a determination of the effect of the processing conditions on the morphological structure and the orientation of particles.

Wednesday 3:35 Ballroom C HS18

A hybrid continuum-lattice dynamic self-consistent field model for nanocomposite fluids

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We present a hybrid continuum-lattice (HCL) approach for modeling the dynamics of anisotropic filler nanoparticles in multiphase fluids under applied stresses. Our method couples off-lattice Newtonian time evolution of the center-of-mass position and orientation of anisotropic filler particles with a dynamic self-consistent field (DSCF) lattice model for the dynamics of inhomogeneous molecular and polymeric fluids. Continuous positions and orientations of

particles off-lattice are represented by lattice averages of solid-fluid boundaries. Particle motion generates mass, species and momentum transport in the surrounding fluid by means of the DSCF solid-fluid boundary conditions. Conversely, the total stress at the particle boundaries, obtained from the DSCF evolution equations, generates the forces and torques needed as input for the off-lattice Newtonian evolution of the particle center-of-mass position and orientation.

We will present initial results of applications of this HCL-DSCF method to simulate the dynamics of anisotropic nanoparticles in inhomogeneous molecular fluids. Extensions of the HCL-DSCF approach to model the dynamics of polymer nanocomposite fluids with anisotropic filler particles will be discussed.

Wednesday 4:00 Ballroom C HS19

Elastic effects in polydispersed acrylic latexes

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Particle to particle interaction dominate in concentrated dispersions resulting in a complex microstructure due to ordering of particles. Extent of ordered and disordered regions in a microstructure depends on the magnitude of shear rate (Peclet number). Flow fields influence collisions of particle to particle which are subject to Brownian, hydrodynamic, electrostatic and van der Waal forces moving a dispersion from having a dominant ordered structure to a disordered structure and then eventually into a dominant ordered region in the dispersion.

Polydispersed particles of acrylic latexes were treated to both steady and oscillatory shear and their shear response was analyzed to determine shear rate dependence, yield stress and static elastic modulus. The aggregate particles stemming from primary particle form fractal-like structures, which coupled with volume fraction of particles, relate to correlation length of the network. By considering chains from a bundle of primary particles in a network undergoing creation, evolution and annihilation, stress and relaxation modulus can be calculated with relaxation time constant as dependent on fractal size and volume concentration. The shear modulus and relaxation time constant from dynamic experiments are calculated and their dependence on aggregate size is determined and compared to network models.

Wednesday 4:25 Ballroom C HS20

The role of porosity on the rheology of silica dispersions

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Extensive studies of the structure of the electric double layer, particle interactions and dispersion stability in the presence of ions, are available from the literature, for dispersions of solid silica particles. It is also possible to find information on the rheology of such systems. However, the influence of porosity on the rheological behavior and its relationship with the underlying physico-chemical properties of the particles remains comparatively unexplored. This work deals with the understanding of the flow properties of polydisperse, porous silica dispersions as a function of silica concentration, particle size, porosity profile, pH and electrolyte. The dispersions were thoroughly characterized for particle size, shape, hydrated density, pycnometry, surface area, porosity, refractive index and acoustophoretic mobility. The rheology study consisted of a viscometric and an oscillation analysis, either in controlled stress or controlled strain mode. A variety of geometries were investigated. The system was studied as a function of the concentration of silica in a solution of sodium or potassium chloride. The results showed: - The apparent Bingham yield and the plastic viscosity were found to be influenced by the measuring geometry - The Bingham yield stress went through a maximum around pH 7.0, as a function of pH, for both salts. Interpretation: the interactions between the flow units were tentatively described by a pair potential analysis at a given silica volume fraction and as a function of salt type, concentration and particle porosity. The controlling parameters were: the Hamaker constant of the porous silica and the variation in the electrokinetic potential with pH. It proved possible to draw a map of "stability-instability" zones as a function of the pH of the dispersion. Regions of differing aggregation states were achieved by adjusting the pH and this was consistent with the peak in the yield stress.

Wednesday 4:50 Ballroom C HS21

Rheology of highly concentrated particle-liquid systems

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A number of industrial applications employ suspensions formulated with non-colloidal particles in non-Newtonian carrier fluids, such as those used in oil service industry to facilitate rapid transport of sand from floating vessels to stationary offshore platforms. They also find application in the transport of drill cuttings from barges to land based processing facilities. The goal in each of these applications is to maximize solids transport rate by using the largest solids concentration possible while maintaining a high level of pumpability. Very little is known about flow properties of these suspensions as solids concentration approaches maximum allowable volumetric fraction. An investigation of these flow properties was undertaken using a customized parallel plate rheometer uniquely suited for granular systems. The rheometer is designed to apply a specific volumetric strain or degree of compaction while shear and normal stresses are being measured. Flow properties of numerous granular materials were measured under varying degrees of compaction in the presence and absence of lubricants. Both hydrocarbon and aqueous base lubricants were evaluated at concentrations ranging from below to slightly over the saturation value for granular media. A novel approach for modeling stress-strain rate relationships as a function of particle and fluid properties is described. Particle variables investigated include surface morphology, size, shape, and density. Fluid properties are characterized in terms of non-Newtonian viscosity parameters and viscoelastic parameters such as storage and loss moduli and complex viscosity. The model simulates the dynamic friction created by closely packed spheres rolling and sliding in shear fields while being lubricated by an interstitial fluid. Rheometer results are correlated with pipe flow data to estimate hydraulic friction behavior. The resulting model provides valuable insight to the design of novel "particle-fluid" systems as well as equipment design.

Wednesday 5:15 Ballroom C HS22

Yield stress and wall slip phenomena in colloidal silica gels

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Evidence of wall slip and magnitude of yield stress are examined for colloidal gels consisting of hydrophobic silica, polyether, and lithium salts using geometries with serrated, smooth, hydrophilic and hydrophobic surfaces. In the absence of wall slip with serrated plates, different methods of measuring yield stress are compared: conventional extrapolation of shear stress in steady shear experiments and dynamic experiments at large strain amplitudes. In the latter, the yield stress is denoted by the maximum in the elastic stress, the product of the elastic modulus and strain, when plotted as a function of strain amplitude. Although excellent agreement is observed in the yield stress values using both these techniques, the dynamic method seems preferable considering its experimental ease, accuracy and lack of extrapolation. In the presence of smooth geometries, the silica gels show evidence of wall slip with a concomitant decrease in yield stress. Using underestimation of yield stress as a measure of wall slip, we find slip to be unaffected by changes in gel modulus obtained through incorporation of additional silica or salts. The use of smooth surfaces compared to serrated surfaces leads to approximately a 60% reduction in yield stress for all such samples. However, increase in solvent medium viscosity, through use of different polyethers, reveal a decrease in slip. To investigate further the slip phenomena, we have created plates with different surface energies. The use of hydrophobic plates reduces slip significantly and produces data comparable to that with the serrated plates. The hydrophilic plates have minimal effect on slip and produces data analogous to that obtained using smooth plates. These results can be explained based on the fact that the particle-lean layer, responsible for slip, remains so with hydrophilic plates as it repels the hydrophobic silica particles in favor of the polar solvent. In contrast, the hydrophobic silica interacts with the hydrophobic plates, thus reducing slip.

Symposium VP
Viscoelasticity of Polymer Liquids

Organizers: Jay Schieber and Shi-Qing Wang

Wednesday 1:30 Ballroom D VP6

Dielectric response of liquid polymers in oscillatory shear flow

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A variation of dielectric properties of material with deformation is called electrostriction. This effect resembles a well-known birefringence phenomenon. Moreover, birefringence is a manifestation of electrostriction in optical range of electromagnetic spectrum. Because electrostriction can be observed in both constant and wide range of alternating electric fields, the measurement of electrostriction provides shear and normal stress/strain distribution in solid and liquid polymers as birefringence does but is not limited to transparent materials, requires much simpler data acquisition techniques, can be implemented for in-line monitoring of polymer processing and can be easily combined with rheological measurements. In this talk, we will present electrostriction and rheological testing of various liquid polymers and polymer composites in oscillatory shear flow. A dielectric response due to shear electrostriction is measured for the frequency of oscillation and the double frequency of oscillation (called the first and the second harmonics). Electrostriction response is compared with loss and storage shear modulus obtained for the same polymers. We will discuss a relationship between electrostriction data for the first and the second harmonics and viscoelastic properties of the polymers. Our results indicate that shear electrostriction response varies with frequency and amplitude of the oscillatory-shear deformation, as well as composition and a degree of cross-linkage of the polymers. A theoretical interpretation of obtained experimental data will be provided. Potential impact of the shear electrostriction effect to study liquid polymers and in-line monitoring of polymer processing will be discussed.

Wednesday 1:55 Ballroom D VP7

Mechanical hole burning spectroscopy: A comparison with dielectric non-resonant spectral hole burning

Xiang Fu Shi and Gregory B. McKenna
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Dynamics in complex fluids is currently a subject of intense interest. One particular aspect of current research activities is the investigation of spatial and dynamic heterogeneity and their interrelationships. Here we look at a fundamental method referred to as non-resonant spectral hole burning (NSHB) and analyze the dielectric methods with a mechanical analogue. A mechanical hole-burning scheme was constructed to compare the analogous observations to those from dielectric non-resonant spectral hole burning (NSHB). In NSHB the material is subjected to a large sinusoidal "pump" followed by a small step "probe". Deviations from simple linearity have been interpreted as evidence of heterogeneous dynamics. Here we use the K-BKZ nonlinear viscoelastic constitutive equation, which invokes no explicit heterogeneity, to examine what aspects observed in the dielectric measurements can be explained as simple non-linearities and which cannot. It is particularly interesting to note that the nonlinear constitutive model in the simplest form of a time-strain separable kernal function cannot reproduce the hole-burning phenomenon, although some features of NSHB can be reproduced when time-strain separability is suppressed. Our results also suggest that mechanical NSHB could be a useful tool for investigating the nature of the nonlinear response of polymers, both in the melt and glassy states. e.g., how does time-strain separability or its breakdown affect mechanical NSHB measurements and can mechanical NSHB provide insight into the nature of the polymer and glassy dynamics.

Wednesday 2:20 Ballroom D VP8

Further implications and applications of HN viscoelasticity modeling

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An introduction to modeling linear viscoelastic properties of polymer melts with the Havliliak-Negami (HN) functional form has recently been given elsewhere. In this sequel, we consider how the phenomenological HN model applies to prediction of non-linear viscoelastic properties from measurements of linear ones. Insertion of HN relaxation spectra, derived from fitting complex viscosity data, into an elongational viscosity expression based on a truncated K-BKZ constitutive equation gives predictions that are much better than are given by discrete-mode relaxation spectra resulting from conventionally fitting the same data. For materials that are well described by HN models, it is easy to reach conclusions about the applicability of several traditional rules of thumb, such as Gleissle's mirror rules, the second Cox-Merz rule, and Wagner's approximation for the first normal stress coefficient. Related formulas of Laun and Tanner for normal stresses and extrudate swelling are also readily evaluated in combination with HN models. Wide applicability of the HN model to both linear and nonlinear viscoelastic behavior strongly recommends it over many more-traditional forms.

Wednesday 2:45 Ballroom D VP9

Material function predictions of stochastic rheological model

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A stochastic rheological model for polymeric fluids is discussed. The model combines aspects of microscopic models with continuum mechanics. The dynamics of the macromolcules is described by two independent Gaussian random variables, or vectors, which can be interpreted within the frameworks of network theory and reptation theory. The expression for the polymeric stress tensor is given as a function of these dynamics, which involve two strain functions similar to those in factorized Rilvin-Sawers model.

The predictions of the model in various rheometric flows are presented for a low-density polyethelene (LDPE) and a polyisobutylene (PIB) solution. Specifically the start-up of steady shear flow, steady shear flow, step strain (stress relaxation after sudden displacement), stress relaxation and elongational flow are considered. Comparisons of the model predictions which are obtained by using stochastic simulations and available experimental data are made on the LDPE and PIB solution. We find that the model predicts well the qualitative and quantitative behavior of these materials. Finally, various model modifications are discussed.

Wednesday 3:35 Ballroom D VP10

Finite step rate corrections in stress relaxation experiments: A comparison of two methods

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The material response after a constant strain rate followed by a constant strain differs from the response to an ideal step to a constant strain at short test times. Due to experimental limitations, the ideal step-strain cannot be achieved. As a result, short time stress relaxation data has to be corrected in order to obtain reliable estimates of, e.g. the modulus $G(t)$, at times shorter than approximately ten times the ramp time. Assuming a relaxation modulus of the form, $G(t)=G_0\exp(-(t/t_0)^b)$, we compare two methods of correction to the stress relaxation data obtained after a linear ramp. Lee and Knauss used an iterative scheme based on Boltzmann superposition. We compare this with the Zapas-Craft approach in which the "true" relaxation time becomes t-$t_1/2$ (t is the experimental time and t_1 is the finite time to apply the step in strain). Although t-$t_1/2$ provides a better correction for "true" times just slightly greater than $t_1/2$, only the Lee-Knauss model can be used for times shorter than $t_1/2$. We find that the difference between responses obtained from the simulation of the ramp to strain and the true strain response is approximately 6.5% at t_1. The difference is less than 0.5% after the Lee-Knauss correction. We also compare results from both correction methods on the shape of the corrected curve by comparing G_0, b and t_0 obtained by curve-fitting the corrected curves with the input parameters to the above equation. Numerical computations show that when the relaxation time is short, there is a substantial error in the Lee-Knauss correction. We will also discuss the case for which the ramp-step is replaced with a more realistic function. Also, it is often desirable to have a similar correction available for large deformation responses. However, the Lee-Knauss method is valid only for linear viscoelastic systems and the Zapas-Craft

approach has not been rigorously evaluated for large deformations. We examine the possibility of extending the latter within the context of the BKZ single integral model.

Wednesday 4:00 Ballroom D VP11

Topological effects on viscoelastic quantities in polyethylene resins

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The subtle effects of long-chain branching on the rheological properties of polyethylene resins have been an area of great interest during the past decade. Most of this interest has stemmed from the development of homogeneous, single-site metallocene catalysts. In the present study, a series of metallocene and conventional polyethylenes are investigated to better understand the sensitivity of various viscoelastic quantities to the presence of long-chain branching. The sparsely branched metallocene resins exhibit a greater degree zero-shear viscosity enhancement and an earlier onset of shear thinning when compared to linear analogs. Furthermore, the zero-shear viscosity dependence upon long-chain branching among all polyethylene resins shows excellent agreement with the empirical predictions of Janzen and Colby (1999). Surprisingly, the primary normal stress differences and extensional viscosities of the sparsely branched MCPE resins are not as sensitive to long-chain branching as the conventional LDPE resin. This implies that these two quantities more directly scale with long-chain branch content than the shear viscosities.

Wednesday 4:25 Ballroom D VP12

Phase behavior and rheology of blends of hyperbranched polystyrene and polyvinyl methyl ether: Effect of architecture

Rangaramanujam M. Kannan and Semen Kharchenko
Chemical Engineering and Materials Science, Wayne StateUniversity, Detroit, MI 48202

Linear polymers and hyperbranched polymers represent two ends of branching complexity. To understand the role of architecture on the rheology, we are studying polystyrene melts with architectures varying from linear, symmetric star, to hyperbranched. We have synthesized star-like hyperbranched polystyrenes (HBPS) of varying arm length (from 10,000 to 50,000 g/mol) and number of arms (approximately 20 to 50). Simultaneous GPC, light scattering and intrinsic viscosity measurements suggested that these HBPS materials have a 'compact' structure with a high density of arms.

Rheological and rheo-optical properties of the hyper-branched polymers are compared with those of linear and symmetric star polystyrenes. Our results suggest that the homopolymer HBPS melts show a significant failure in the stress-optic rule, characterized by a sharp increase in the stress-optical coefficient at 'low frequencies' and high temperatures. This suggests that there may be a soft-core in these materials due to preferential orientation of parts of chains near the center. The predominantly elastic response of the soft structures may be responsible for the enhanced birefringence. Our results show that these materials may exhibit both polymeric and soft-colloidal nature. Blends of linear PS and HBPS with polyvinyl methyl ether (PVME) show the role of high branch density on the phase behavior and rheology. The for the same total PS molecular weight, kinetics of phase separation appear to be significantly slower for the HBPS/PVME blend. At comparable compositions in the miscible state, the HBPS/PVME blends show thermorheological simplicity, where as the linear PS/PVME blend shows thermorheological complexity. Our current results are viewed with the perspective of the HBPS being a 'soft-colloidal' particle suspended in a PVME matrix for most compositions. Rheological and mechanical data will be presented and discussed both in the miscible and the immiscible state.

Wednesday 4:50 Ballroom D VP13

Rheology and orientation behavior of metallocene-catalyzed semi-syndiotactic polypropylenes: Role of tacticity

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Understanding the relationships between tacticity and morphological behavior in semicrystalline polymers is vital for their processing, and product engineering. Metallocene catalysts allow for control of tacticity in polyolefins, making it possible to synthesize materials with a wide range of properties from a single monomer. We are studying syndiotactic polypropylenes (s-PP) with varying degrees of 'syndiotacticity', ranging from nearly atactic to nearly syndiotactic. These materials have been custom-synthesized using asymmetric, bridged cyclopentafluorenyl catalysts, and characterized using NMR, modulated DSC, mechanical testing, AFM, rheology, and rheo-optical FTIR spectroscopy.

Quantitative mechanical and linear dichroism spectral responses to applied tensile deformation are measured simultaneously using the rheo-optical FTIR apparatus. This apparatus allows us to monitor deformation-driven morphology changes and molecular orientation associated with crystalline and amorphous domains simultaneously. In liquid-nitrogen-quenched solid-state films of highly syndiotactic (~ 90 % rr) polypropylene, tensile deformation appears to have a strong influence on the crystalline morphology and orientation beyond the yield point. By tracking characteristic IR absorbance and the IR dichroism spectra, we are able to observe the initial (post-quench) presence of helical chains (at 812, 868, 977, and 1005 cm^{-1}) and their gradual transformation into a trans-planar configuration (963 and 1131 cm^{-1}) beyond the yield point. In contrast to the highly syndiotactic PP, semi-syndiotactic polypropylenes exhibit a 'para-crystalline mesophase' when quenched from the melt. This 'mesophase' that slowly grows as the sample ages at room temperature. AFM and infrared linear dichroism (IRLD) are used both to monitor the time evolution of the mesophase (at 824 and 900 cm^{-1}) and to define its influence on mechanical properties. The semi-sPPs show a significant amount of melt and solid state elasticity.

Wednesday 5:15 Ballroom D VP14

An algebraic constitutive equation for complex flows of viscoelastic liquids

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Non-Newtonian materials exhibit different behavior when submitted to shear or extension. A constitutive equation in which the stress is a function of both the rate of deformation and the type of the flow is proposed and analyzed. The analysis unfolds the assumptions that are needed to obtain the equation starting from a constitutive model for extra-stress tensor which has a perfect instantaneous memory. The proposed equation combines information obtained in shear, extension and rigid body motion to predict the stress as a function of the local flow type in a complex flow. It is also shown how to predict Trouton ratios larger than three for inelastic liquids such as suspensions of rigid non-spherical particles in a Newtonian solvent. One feature of the model is that all the steady-state rheological functions in simple shear flow and in extensional flow are predicted exactly. Another important feature that is included is the split of the extensional viscosity into two terms: a dissipative term, which is related to the shear viscosity, and an elastic term, which is related to the first and second normal stress coefficients. The implications of the proposed splitting with respect to the second law of thermodynamics is discussed. The equation is employed to obtain finite-element numerical solutions for the flow through an axisymmetric 4:1 abrupt contraction. The Couette correction, vortex intensity, and vortex size are obtained for different combinations of values of two dimensionless numbers. These dimensionless parameters are both ratios between elastic and viscous forces, but one, which we call the Deborah number, is related to shear-flow elastic effects, while the other, called here Weissenberg number, is related to extensional-flow elastic effects. These numerical results show that the dependence on these dimensionless numbers is such that vortex intensity increases as the value of either number is increased, while Couette correction is observed to depend oppositely on these parameters.

Thursday Morning

Symposium SC
Stiff Chains: Biopolymers, Polyelectrolytes, and LCPs

Organizers: David Morse and Guy C. Berry

Thursday 8:05 Ballroom A SC1

Oscillatory stress responses of polymers in the nematic phase

Elvira Somma[1], Jan Vermant[1], Paula Moldenaers[1], Massimiliano Grosso[2], and Pier Luca Maffettone[3]

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In this work the transient rheological behavior of a lyotropic liquid crystalline polymer, PBLG in m-cresol (c ~ 12%) has been studied experimentally in the transition region between the "tumbling" and the "flow-aligning" regime. The evolution of the first normal stress difference (N_1) was measured to determine the point of where N_1 is at its negative maximum. The samples were subjected to different transient experiments in a narrow shear rate region around this negative maximum. Both flow reversal experiments and step-down experiments were performed. Whereas previous research focused on the initial transient behavior, here the long-time evolution of the stresses was monitored. This required high data sampling rates over a prolonged period in order to get all the details of the oscillatory response. Both the shear and the first normal stress difference show an oscillatory profile that seems not to dampen in time. Moreover, the stress signals, studied with Fourier analysis (FFT and Lomb Periodograms), showed that the oscillatory responses are characterized by two distinct frequencies in some flow conditions. The results will be compared with predictions from the rigid-rod model.

Thursday 8:30 Ballroom A SC2

Shear-induced alignment of smectic side-chain liquid crystalline polymers

Stanley Rendon[1], Wesley R. Burghardt[1], Maria L. Auad[2], and Julia A. Kornfield[2]

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It is well recognized that large amplitude oscillatory shear is capable of generating macroscopic alignment from an initially random orientation distribution in a variety of complex polymer fluids. Side-group liquid crystalline polymers are particularly intriguing, since the flow field may couple differently to the polymer backbone and the mesogen ordering. We report combined rheological and in situ x-ray scattering investigations of alignment in several smectic side-group LCPs in large-amplitude oscillatory shear. Synchrotron x-ray scattering is used to study orientation development using a rotating disk shear cell that tracks orientation within the flow-vorticity (1-3) plane. In each case, we find that shear promotes 'perpendicular' alignment of the smectic layers, where the lamellar normals line up along the vorticity direction of the shear flow.

Thursday 8:55 Ballroom A SC3

Study of the orientation field and topological defects in a nematic liquid crystal surrounding a spherical particle

Davide A. Hill and Olga V. Sozinova
Chemical Engineering, University of Notre Dame du Lac, Notre Dame, IN 46556

We report on progress in resolving the full structure of a nematic liquid crystal surrounding a spherical particle, with strong homeotropic anchoring and uniform far-field alignment. The orientation field is described in terms of the order-parameter tensor, thereby allowing us to resolve the structure of satellite defects anchored near the particle. We adopt a Landau-de Gennes expansion for the distortional free energy and a molecular free energy expression as given by Doi. The orientation field is obtained numerically by direct minimization of the global free energy. Such a scheme allows us to resolve competing microstructures and evaluate their stability.

In agreement with Frank-elasticity based estimates and molecular dynamics simulations, we find three possible defect/orientation patterns: 1) a "Hyperbolic Hedgehog" (HH) (asymmetric) structure, 2) an equatorial "Saturn Ring" (SR) (symmetric), and 3) an unstable, non-equatorial ring. For strong anchoring, the stability of each pattern depends on particle size.

We shall discuss the problem of mapping the transition from a stable HH pattern to a stable SR structure as the particle becomes smaller than a critical size. Limitations inherent to the Rapini-Popoular description of orientational boundary conditions will also be discussed.

Thursday 9:20 Ballroom A SC4

The effects of hydrodynamic interactions on polymer dynamics in extensional flows

Charles M. Schroeder[1], Steve Chu[2], and Eric S. Shaqfeh[3]
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In his seminal *J. Chem. Phys.* paper (1974), P.G. DeGennes predicted the existence of an abrupt coil to stretch transition for linear polymers in flows with dominant extensional character; furthermore, he commented on the role of intra-chain hydrodynamic interactions in such strong flows. Recently, it has been shown that incorporation of hydrodynamic interactions through an Oseen-like tensor for bead-spring chains in Brownian dynamics simulations has essentially no effect on the transient or steady molecular extension for lambda-phage DNA molecules (Jendrejack, et al., *J. Chem. Phys.*, v. 116, p. 7752, 2002). In the series of experiments presented in this work, we examine the effect of increasing polymer length on chain dynamics by employing "ladders" of lambda-phage DNA. Coupling basic biological concepts with single molecule fluorescence microscopy, we measure the transient and steady dynamics of very long chain polymers in extensional flows. By employing manual feedback control of the stagnation point location in a planar extensional flow, we can probe the dynamics of single chains for very large strains. Finally, a discussion regarding the progress of single molecule fluorescence studies of synthetic polymer systems will be presented.

Thursday 10:10 Ballroom A SC5

Influence of chain stiffness on the relaxation of an initially straight semiflexible polymer

Panagiotis Dimitrakopoulos and Inuka D. Dissanayake
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This study considers the relaxation of a single semiflexible polymer chain in a viscous solvent from an initial straight configuration. Physically this problem may correspond to the case of a polymer chain fully stretched by an (infinitely) strong flow and then relaxed by switching the flow off. This problem is also motivated by recent experiments with single DNA molecules relaxed after being fully extended by applied forces. To study this problem, Brownian Dynamics simulations based on a discretized version of the wormlike model are employed. The properties of the polymer chain are expressed as a function of the chain length and polymer stiffness. In this talk, we will present results which correspond to different biopolymers and different time scales. Comparisons with analytical predictions and experimental findings will also be presented.

Thursday 10:35 Ballroom A SC6

Wavelength-dependent hydrodynamics of a solution of semiflexible rods

David C. Morse

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

I will discuss a theory for the spatially nonlocal viscoelastic response of a semidilute solution of hydrodynamically interacting semiflexible rods, at length scales less than the length of the rods. An effective medium theory for the frequency- and wavelength-dependnt response of such a solution may be constructed by calculating the ensemble averaged drag force exerted by individual rods upon the solvent in a weak but otherwise arbitrary solvent flow field, and using this to self-consistently calculate the flow field produced by a weak external force density. The theory will be applied to the interpretation of microrheology experiments on solutions of filamentous actin, in which the solution is probed by monitoring the motion of beads with diameters that are often much less than the length of the surrounding rods.

Thursday 11:00 Ballroom A SC7

Rheology and single-molecule behavior of semiflexible chains in shear flow

Alberto Montesi and Matteo Pasquali

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We have studied the steady behavior of dilute solutions of semiflexible polymer in shear flow, as well as the dynamics of single chains under these conditions. The polymer molecules are modeled as freely-draining, non-interacting semiflexible wormlike chains; the emphasis is on relatively stiff chains with $L/L_p < 1$, which is the case in many biopolymers. We find that conformational properties of semiflexible molecules in shear flow have a qualitatively different behavior from that of flexible chains; rather than expanding, the radius of gyration of the molecules shrinks and molecules and assume highly bent configurations at large enough value of a dimensionless number representing the ratio between flow forces and bending forces along the chain. The analysis of the onset of molecular shrinking, related to an elastic instability of the driven filaments as they traverse regions of compression while tumbling in shear flow, is presented. 3-D Brownian dynamics simulations are performed, showing that the instability drives the polymer chains also toward the vorticity direction; thus, the end-to-end vector of stiff polymer chains tumbles strongly in the velocity-vorticity plane, unlike the end-to-end vector of flexible polymer, which tumbles only in the velocity-gradient plane. Scaling laws for relaxation time, zero shear viscosity and zero first normal stress difference of semiflexible chains are proposed. We also present a mastercurve for material functions of semiflexible chains, we identify two different power law regimes, a rod-like and a flexible-like regime, and we show the correlation to the dynamics of single molecules.

Thursday 11:25 Ballroom A SC8

Hydrogen bonding and intermolecular interactions in galactomann polymers

Robert K. Prud'homme and Yu Cheng

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Guar galactomannan polymers have unique viscosity versus polymer concentration profiles arising from hydrogen bonding along the mannose backbone. The extent and strength of this hydrogen bonding can be studies using the osmotic stress technique developed by Parsegian. In this study we compare hydogen bonding interactions between substituted and unsubstituted galactomannans and relate it to the viscosity of these systems.

Thursday 11:50 Ballroom A SC9

Fluorescence photobleaching recovery and dynamic light scattering studies of polyelectrolyte solutions

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The diffusion of dilute poly(styrene sulfonate sodium salt) (NaPSS) through concentrated polyelectrolyte matrices has been investigated with an optical tracer method. The tracer diffusion coefficient (*D*) of lightly labeled NaPSS decreased with probe molecular weight. The probe diffusion coefficient also decreased with the concentration of

matrix polymer, but not always indefinitely. In the absence of added salt, *D* stopped declining at a plateau value. With the addition of salt, *D* increased and the plateau disappeared. Also on the addition of salt, a red shift of the fluorescence spectrum and enhanced quantum yield were observed for fluorsceinamine-labeled NaPSS. The extraordinary diffusion regime long observed in dynamic light scattering measurements at low salt was re-investigated using a dialysis cell equipped with a chamber to control salt concentration and pH without adding particulate contaminants or refiltering the solution.

This work supported by the National Science Foundation, Division of Materials Research.

Symposium IR
Interfacial Rheology: Adhesion and Slip

Organizer: Ali Berker

Thursday 8:05 Ballroom B IR1

Strong interactions at wall to generate anomalous wall slip behavior during flows of complex fluids

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The traditional apparent wall slip mechanism involves the lubrication of the walls of the flow channel with an apparent slip layer. The material constituting the apparent slip layer generally exhibits a lower viscosity than the bulk. For example, in flow of concentrated suspensions the liquid binder of the suspension forms the apparent slip layer. For such systems increasing the surface/volume ratio reduces the stresses necessary to drive the fluid. The dependence of the shearing stress on the surface/volume ratio of the flow channel establishes the basis of Mooney corrections for the characterization of wall slip velocity. However, there are dispersions and suspensions which undergo structural or chemical changes, especially through their interactions with the wall material, that increase the shear viscosity of the fluid found at the wall, generating results which are the opposite of what is encountered with the traditional apparent slip mechanism, involving the lubrication of channel wall. Here we will provide three examples of such systems that exhibit such anomalous wall slip behavior. The first system is a ceramic suspension that interacts strongly with metal walls during flow. The second and third systems involve ingredients that undergo significant variation and fracture of their building blocks. For all three systems, the pressure drop necessary to drive the fluid through a slit or capillary die increases with increasing surface to volume ratio of the rheometer and although there is wall slip the traditional methods of determining wall slip do not apply.

Thursday 8:30 Ballroom B IR2

Wall slip in drag flow: A direct rheological measurement

Prashant S. Tapadia and Shi-Qing Wang
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Highly entangled polymeric fluids tend to undergo wall slip when sheared at high stresses. Consequently, capillary extrusion of certain polymers such as linear polyethylene and polybutadiene exhibit spurt flow or stick-slip transition (SST) beyond a certain critical stress of about 0.3 MPa. Wall slip in drag flow is usually preceded by other instabilities such as edge or meniscus fracture and is often not observed, except locally away from the edge. In the present study, polymer solutions are prepared to lower the critical stress for the SST to a level (ca. 10 KPa), below which the meniscus fracture does not occur. The polymer solution under investigation is made of polybutadiene of very high molecular weight to ensure that the solution is sufficiently entangled and capable of displaying a measurable magnitude of wall slip. Unlike capillary flow, the material is being re-sampled continuously during flow in a parallel plate flow cell. Many interesting features show up including a finite induction time for SST at lower stresses, fluctuating shear rate and hysteresis behavior under controlled stress mode and stress fluctuations under controlled rate.

(1) N. Plucktaveesak and S.Q. Wang, "Interfacial flow transition in entangled polymer solutions", Macromolecules 32, 3045 (1999).

Thursday 8:55 Ballroom B IR3

Spurt in extrusion of polymer melts: A stick-slip phenomenon

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Extrusion of polymers may lead to several instabilities. Understanding the microscopic origin of the macroscopic flow behavior is the key to control these instabilities. Although spurt oscillations are quite commonly believed to originate from stick-slip transition in the die land, it is by no means clear how it depends on the polymer characteristics and the physical parameters, like temperature. In this study we elucidate the origin of spurt by an integrated macroscopic-microscopic approach. We exploit the relation between slip velocity and shear stress at the wall to develop a macroscopic model for spurt. Next the compressibility in the barrel is invoked and a two-dimensional singularly perturbed system of differential equations is obtained. From this we demonstrate that it is possible to make (quantitative) predictions about the pulsation frequency and the onset and termination of slip. The dependence of the oscillation frequency on the geometry of the die and the barrel are either in good agreement with experiment or allow readily experimental verification.

Thursday 9:20 Ballroom B IR4

Slip at the interface between polymers under shear: A comparison of DSCF, MD and experimental study

Maja L. Mihajlovic[1], Tak Shing Lo[1], Yitzhak Shnidman[1], Wentao Li[2], and Dilip Gersappe[2]

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Recently, a novel dynamic self-consistent field (DSCF) model has been developed and used to study polymeric fluids under shear. The model combines a self-consistent field (SCF) theory of Scheutjens and Fleer (Scheutjens & Fleer J. Phys. Chem., 83, 1619, 1979) with a convective-diffusive lattice-gas model (Khan & Shnidman Prog. Coll. Polym. Sci., 103, 251, 1997). The chain conformation statistics is generated by the SCF matrix formalism that relates segmental volume fractions to segmental site probabilities and coupled with convective-diffusive transport equations. We applied a DSCF model to study block copolymers at polymer blend interfaces under a simple shear. First we investigated the velocity slip at polymer blend interface, and its dependence on chain length, shear rate and interaction parameter. Then, we studied how the addition of block copolymer to the polymer blend affected the interfacial slip. Both entangled and Rouse chains were taken under consideration. The dependence of velocity slip on block copolymer concentration and chain length was thoroughly studied. The results are compared with those obtained by molecular dynamics simulations and experimental study.

Thursday 10:10 Ballroom B IR5

Viscosity reduction mechanism in high molecular mass polytheylen melt containing a small quantity of thermotropic liquid crystalline polymers

Ping Gao and Chi-kwong Chan

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In this paper, we present a phenomenological model for the viscosity changes in bulk high molecular mass polyethylene induced by the presence of a small quantity of a main chain thermotropic liquid crystalline polymer (TLCP) containing flexible spacers. The model assumes that the polymer melt undergoes a yielding process under the influence of the highly aligned TLCP domains. This yielding occurs at a certain critical centreline velocity independent of capillary die diameter. The flow of the polymer melt is divided into two power law regimes upon yielding, namely, the centre core containing the low viscosity melt induced by alignment assisted by the aligned TLCP domains and the outer region containing the essentially random coil polymer melt. Using this model, we successfully predicted that the apparent shear viscosity of the polymer melt depends on the capillary diameter, with the larger capillary diameter showing much lower viscosity. Additionally, the model also successfully predicts the onset of transition of completion to a fully extended chain flow regime. The model has relevance to other flow systems where flow induced phase transition occurs.

Thursday 10:35 Ballroom B IR6

Squeeze flow of waterborne adhesives on porous substrates

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

Thursday 11:00 Ballroom B IR7

The rheology of microelectronics planarization (polishing)

Maria Ronay
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In microelectronics processing metal or insulator layers are deposited conformally into etched trenches of a substrate, after which there is a need to planarize the surface. Ideally material should only be removed from the up areas and none from the down areas of the pattern; if material is removed from the down areas as well, that leaves post planarization steps behind (dishing), which are not only detrimental due to depth-of-focus issues in subsequent lithography steps, but can also impair device characteristics. Since the down area polishes only if the polishing pad is in contact with it, the question is by what deformation mechanism does the pad extend into the down area of the pattern, in a direction that is perpendicular to the direction of shear. By experiments made in the parallel plate configuration on the ARES rheometer it was found that the torque created by sliding friction between a rotating polyurethane foam planarizing pad and a stationary patterned silicon dioxide wafer in contact creates a large second order tensile normal force in the pad, previously found only during the torsion of bulk specimens (Rivlin, Freudenthal & Ronay). The normal force is a linear function of the square of the torque, as required by second order theory. The rheology experiments were conducted in the dry state furthermore using ceria slurries with and without a polyelectrolyte additive. Complementing the rheology experiments with elaborate polishing experiments the magnitude of the extension of the pad into the down area of the pattern could be estimated, and the conclusion made, that second order extension of the pad brought about by surface shear provides the mechanism for dishing. Discovering that friction creates normal stresses and extensions in a rubbery polymer also provides a new mechanism for friction.

Thursday 11:25 Ballroom B IR8

Surface dynamics in polystyrene films

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Surface segmental motion in monodisperse polystyrene (PS) films was studied by scanning force microscopy in conjunction with dynamic secondary ion mass spectroscopy (DSIMS). The monodisperse PSs with various chain end groups were synthesized by an anionic polymerization method. Surface glass transition temperature, T_g, of the PS films was discerned to be markedly lower than the corresponding bulk T_g, and the decrement of surface T_g from the bulk value was strongly dependent on the number-average molecular weight, M_n, and chain end structure at a given M_n. Applying time-temperature superposition principle to the surface segmental motion, the apparent activation energy was evaluated to be 230±10 kJ/mol, being much smaller than reported bulk values. The activation of the segmental motion at the PS surface was explained in terms of chain end effect and reduced cooperativity. Also, the enhanced surface mobility of the PS films was examined on the basis of interdiffusion experiments at temperatures above and below the bulk T_g. DSIMS revealed that the interfacial thickness of the PS bilayer was

monotonically increased with the annealing time and then remained to be a constant in the case of the annealing below the bulk T_g. This result implies that there is a gradient of T_g in the surface region, and makes it clear that the interdiffusion of PS chains can occur even at a temperature lower than the bulk T_g.

Thursday 11:50 Ballroom B IR9

Interfacial rheology of graft-type siloxane surfactants

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The viscoelastic properties of graft-type siloxane surfactants at the silicone oil/water interface were investigated with an interfacial stress rheometer (ISR). This study is of importance since these graft-type siloxane surfactants are effectively used in the personal care industry as water-in-silicone oil emulsifiers. The mechanism in which these surfactants stabilize water-in-silicone oil emulsions seems analogous to a Pickering emulsion. For Pickering emulsions, solid particles like silica or clay preferentially aggregate at the oil/water interface forming a solid-like barrier, which can resist coalescence. Similarly, in the presence of silicone oil and water, these graft-type siloxane surfactants form spherical particles of a surfactant-rich phase. These surfactant-rich particles act like the solid particles in a Pickering emulsion, forming a solid-like network at the silicone oil/water interface that opposes coalescence. The effects of different emulsion formulation parameters, such as surfactant concentration in the oil phase as well as the chemical structure of the surfactant, on the interfacial rheological properties were studied with the ISR. The viscoelastic properties of the interface are inherently connected to the formation and aggregation of these surfactant-rich particles at the silicone oil/water interface. Consequently, measuring the effects of different formulation parameters on interfacial rheology can be used to study their effect on the formation of these surfactant-rich particles.

Symposium HS
Heterogeneous Systems: Suspensions, Composite, and Multiphase Materials

Organizers: Daniel De Kee and Yuntao Hu

Thursday 8:05 Ballroom C HS23

Rheological properties of concentrated fiber suspensions in polymers

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The rheological behavior of a commercial short glass fiber filled polypropylene and of model suspensions of the same fibers in polybutene and in a Boger fluid has been studied. All types of suspensions were shown to exhibit stress overshoots in creep and in stress growth experiments. Under flow reversal, a smaller overshoot of smaller amplitude was observed, at a larger deformation compared to the primary overshoot. The reversal overshoot has been attributed to tumbling of fibers that are not totally aligned with the flow direction even after a very long time. A large overshoot was also observed for the primary normal stress difference in stress growth experiment. Under flow reversal, the normal stress took initially negative values and depicted a smaller positive overshoot before reaching a steady-state value. The negative normal stress has been attributed to non-affined deformation. Two models have been used to simulate the reversible viscosity overshoots. One of them is based on the Folgar-Tucker equation for fiber motion and on the Lipscomb's constitutive equation. The equation has been empirically modified to include a slip parameter to account for fiber-fiber interactions and non-affined deformation. The other one, an extension of the Folger-Tucker equation has been theoretically modified to account for non-affined deformation. Experimental data for concentrated fiber suspensions in a polypropylene and in a polybutene have been compared to both model predictions and a good agreement has been obtained.

Thursday 8:30 Ballroom C HS24

Effects of the specific energy input during mixing and the resulting degree of mixedness on the rheological behavior of concentrated suspensions

Christos Tsenoglou, Dilhan M. Kalyon, and Elvan Birinci
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The rheological behavior of concentrated suspensions, filled with rigid particles, depends on the microstructure of the suspension, including the distributions of the particle size, shape and concentrations of the rigid particles. During the mixing process changes in the sizes and the shapes of the particles, which are being wet and coated by the binder, result in significant changes in the rheological behavior of the suspension. It is generally difficult to follow these changes along with the rheological behavior of the evolving suspension. Here we will present results with an electrically conductive suspension (a thermoplastic elastomer filled with graphite particles) for which the rheological behavior and the degree of the mixedness of the ingredients were simultaneously determined to allow inferences to be made on the sizes of the particles and their instantaneous maximum packing fraction versus the specific energy input incorporated into the suspension during the mixing process on one hand and the volume resistivity of the conductive composite on the other hand. For the degree of mixedness analysis a wide-angle x-ray diffraction technique was used and the specific energy input was obtained upon the integration of the torque on the mixer blades that could be measured. The results emphasize the importance of obtaining a detailed understanding of the behavior such structure sensitive suspensions and the role played by rheological characterization on developing this requisite understanding.

Thursday 8:55 Ballroom C HS25

Rheophysical investigations into natural mud suspensions

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Most materials involved in natural gravity-driven flows in mountainous areas are made up of solid particles within a wide range of sizes in a Newtonian fluid (air or water). When natural suspensions can be tested with the usual laboratory rheometers, they exhibit a wide range of bulk rheological properties (time-dependent effects, viscoplasticity, etc.) and flow effects (particle migration, shear localization). Such properties are difficult to understand and describe within the framework of continuum mechanics most often used for this purpose. A rheophysical approach is an alternative and useful way of describing the dynamics of geosuspensions. Here, we are interested in determining the bulk behavior of a colloidal dispersion in which noncolloidal coarse particles are included. Experiments were performed with kaolin, bentonite, and natural clays (samples collected on a debris flow deposit). Plastic properties were investigated using slump-test experiments, which provided evidence that bulk yield stress resulted not only from the properties of colloidal particles but also from jamming effects in the arrangement of coarse particles. Then, using flow visualization techniques (magnetic resonance imaging) and a coaxial cylinder rheometer, we found that the experimental flow curve contrasted significantly with the behavior of an ideal yield stress although, if we only considered the flow curve derived by using the conventional rheometrical treatment, it was possible to fit a Herschel-Bulkley to the data. Notably it was observed that the velocity profile close to the yielding surface was not smooth, as predicted by a Herschel-Bulkley model, but discontinuous. This did not originate from migration of the coarse particles since a similar behavior was also observed when the coarse particle content was zero. Moreover a steady flow was observed provided that the shear rate exceeded a critical value.

Thursday 9:20 Ballroom C HS26

Rheology and order in acicular ferromagnetic dispersions

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A constitutive model for dispersions of acicular magnetic particles has been developed by modeling the particles as rigid dumbbells dispersed in a solvent. The effects of Brownian motion, anisotropic hydrodynamic drag, a steric force in the form of the Maier-Saupe potential, and most importantly a magnetic mean-field potential are included in the model. The development is similar to previous models for liquid-crystalline polymers. The phase behavior is studied in terms of an orientational order parameter S and an average polarity parameter J. A numerical solution

technique involving an expansion in terms of spherical harmonic functions is employed. The resulting predicts a rich variety of rheological and structural behavior. A transition from isotropic to nematic phases at equilibrium is predicted. Rheological predictions for dispersions initially in isotropic equilibrium compare well with experimental data for magnetic inks. Multiple phases- stationary as well as periodic- are predicted in the presence of steady shear flow and magnetic field for dispersions initially in nematic equilibrium.

Thursday 10:10 Ballroom C HS27

P-V-T and relaxation characteristics of PP, LC-copolyester and their blends at high pressure

Ernst I. Frenkin, Valery G. Kulichikhin, Vadim E. Dreval, Elena V. Kotova, and Valery N. Kuleznev
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At thermoplastics processing the presence of LC polymers causes significant decrease of viscosity and increase of their strength. The paper contains the results of studying P-V-T characteristics of PP and LC-copolyester PET/HBA (35/65) blends and their mechanical and relaxation properties after injection molding. The experimental results are compared with the theoretical predictions. It is shown that at the temperatures corresponding to the solid or melt states of the blends their thermophysical characteristics change additively with their composition. In the intermediate temperature range the peculiarities of the specific volume, thermal expansion coefficient and compressibility changes vs. temperature are determined by structural and relaxation transitions of the blends components. As a result the PP crystalline structure change may be expected in the course of the blends processing at high temperatures. The modulus of elasticity and the shrinkage of the samples obtained by injection molding were studied. The usefulness of application of the LC-copolyesters for regulation of mechanical characteristics and decreasing of the shrinkage of the specimens obtained by injection molding was found. The comparison of the experimental shrinkage with the one obtained with the use of the Spenser and Gilmore equation shows their difference in 1.5-2.5%. Thus, preliminary the shrinkage values and the prediction of shrinkage decrease of the blends under investigation can estimated by means of calculations.

Thursday 10:35 Ballroom C HS28

Dielectric spectroscopy of blends with a liquid crystalline dispersed phase

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The dielectric loss spectra of blends of low molar mass liquid crystals dispersed in a matrix of polydimethylsiloxane exhibit a peak that can be identified with the presence of the interface. The liquid crystals studied were 4'-pentyl-4-biphenylcarbonitrile (5CB), which exhibits nematic and isotropic phases, and 4'-octyl-4-biphenylcarbonitrile (8CB), which exhibits smectic, nematic, and isotropic phases. The characteristic frequency of this new peak corresponds to the frequency for droplet interfacial mechanics in the linear viscoelastic spectrum. The frequency and the magnitude of the interfacial peak are temperature dependent, and both functionalities exhibit a transition as the dispersed phase passes from smectic to nematic to isotropic, indicating a strong interaction between the structure of the dispersed phase and the interface.

Thursday 11:00 Ballroom C HS29

Evolution of structure in electro- and magnetorheological fluids from a continuum perspective

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The evolution of nonuniform particle concentration distributions in electro- and magnetorheological fluids is described from a continuum perspective. Motion of the particulate phase is described by a particle conservation equation. This equation contains a particle flux, which is related to the particle contribution to the suspension stress. Stability analyses of the particle conservation equation predict the formation of columnar aggregates aligned with the applied field in quiescent suspensions, and formation of particulate stripes aligned with the flow direction in

sheared suspensions, as commonly observed experimentally. Hydrodynamic contributions to the particle flux are relatively unimportant for describing the initial evolution of structural changes from a uniform suspension, but are crucial for the prediction of steady-state structures. At long times, a balance of electrostatic (or magnetostatic) and hydrodynamic stresses determines the details of the patterns formed, e.g., the particle concentration in the stripes. The particulate stripes are predicted to become more dense with decreasing shear rate. Nonlocal contributions to the electrostatic (or magnetostatic) stress do not alter the stability limit, but do play a role in stripe evolution at large times.

Thursday 11:25 Ballroom C HS30

Metal particulate dispersions for data storage applications: Characterization as a function of polymer ratio and pigment volume concentration

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Metal particulate dispersion mill bases are probed with oscillatory shear strain and frequency sweeps as a function of polymer ratio and magnetic pigment volume concentration. These data are scaled in order to elucidate both the general response features of these colloidal dispersions and the specific effects of changing the polymer ratio at the same pigment volume concentration. We assume that changing the polymer ratio while holding the magnetic pigment volume concentration constant changes the magnitude of the attractive interaction potential. The presented data are consistent with this assumption. Magnetic attractive forces between units-of-microstructure predominate in these dispersions and can only be mitigated by physical separation.

Magnetic field-based measurement devices also yield useful information. One such device, a low field (i.e., the magnitude of the applied magnetic field is less than the coercivity of the pigment) pulse field magnetometer (PFM), probes the physical rotation of magnetic units of microstructure in a way that is directly analogous to a creep/recovery test. In the PFM a square wave magnetic field pulse is applied to the dispersion for 125 microseconds and the resulting magnetization monitored as a function of time. As the polymer ratio in the dispersion increases (i.e., the magnitude of the attractive interaction potential decreases) the maximum measured magnetization increases indicating that more of the magnetic units of microstructure are aligned in the applied field direction, i.e., the 'resistance' to alignment is decreased. The relaxation coefficient, a time-scale measure of the initial rate of decrease in magnetization after removal of the applied magnetic field, also increases with polymer ratio. This implies that the initial driving force for 'relaxation' (i.e., the 'disorientation' of oriented magnetic units of microstructure) diminishes as the polymer ratio increases.

Thursday 11:50 Ballroom C HS31

Formulation effects on magnetic mix microstructure

Andrei Potanin and Neal K. Nelson, Jr.
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Steady and oscillatory shear rheological, magnetic susceptibility and particle size measurements are used to characterize the microstructure of metal pigment dispersions in organic solvents with respect to changes induced by milled-in polymer only and polymer + dispersant. An hierarchical structure built of inseparable clusters, aggregates with their size fixed during mix preparation, and a volume-filling network of these aggregates is consistent with our observations. As polymer-to-pigment ratio and/or number of active groups in the polymer increase, the aggregates decrease in size and the network becomes weaker and less brittle. For each polymer-to-pigment ratio an optimum level of dispersant is established. Below the optimum dispersant level aggregates are too large, while above it aggregates appear to interact too strongly. A plateau at intermediate shear rates occurs unless an optimum dispersant level is maintained along with sufficient polymer. This plateau is attributed to wall-slip and may be used to discriminate dispersion quality.

Symposium SM
Rheology at the Sub-Micron Scale

Organizers: Matteo Pasquali and James Harden

Thursday 8:05 Ballroom D SM1

Measurements of rheological and structural properties of thin lubricant films at high shear rates

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Understanding the rheological and structural properties of systems of long-chain molecules in thin films presents fundamental challenges and yet is of immense technological importance. Most common, experimental techniques available for studying the rheological and structural properties are cone-plate and Couette geometries. However, these techniques are limited to moderate shear rate because of the difficulty in removing the viscous heat. A home-built, high shear rate parallel-plate rotational rheometer has been used for measurements of rheological and structural properties of lubricant films confined to sub-micron thin films. The design is similar to a hard disk drive; a thin film is sheared between optically transparent disc and slider. While the rheological properties of the polymer thin film can be obtained from the stresses on the slider, small-angle light scattering and other optical techniques can investigate the sample structure. The film thickness is monitored, in-situ, using a capacitive method. Perfluoropolyether lubricant films have been used to test the apparatus and investigate the rheological and structural properties of the films.

Thursday 8:30 Ballroom D SM2

The structure and dynamics of particle monolayers at a liquid-liquid interface subjected to flow

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The effect of flow on the structure and dynamics of monodisperse spherical polystyrene particles suspended at the interface between decane and water was observed. The presence of strong dipole-dipole repulsion, induced by asymmetric ionization of surface sulfate groups, between the particles in the system results in their arrangement on a hexagonal lattice when at rest. Subjecting the interface to extensional flow, however, causes the lattice structure to pass through a liquid-like state as flow is first applied and finally to a new semi-ordered, anisotropic state during steady flow. This semi-ordered state is oriented and stretched in the flow direction relative to the original hexagonal structure. Although the dynamics exhibited by particles under extensional flow depend on interfacial concentration and strain rate, two very distinct behavioral regimes are observed while under shear flow. At low particle concentrations or high shear rates, nearest neighbors in the lattice align in the flow direction and create strings of particles that slip past each other fairly readily. However, at high concentrations or low shear rates, the interparticle forces gain importance and tend to more strongly keep the particles in their lattice positions. As a result, domains within the lattice are forced to rotate, thus giving rise to movement of particles perpendicular to the flow direction.

Thursday 8:55 Ballroom D SM3

DNA fragmentation via contraction flow

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Contraction flow has been used at the Stanford Genome Center to fragment DNA chains for sequencing and cloning purposes. Contraction flow takes advantage of the high extensional component of the flow to stretch and

subsequently break chains when the flow induces high enough tension along the chain. Experimental work suggests cleavage occurs at C-O bond at C3 carbon (Oefner et al, 1996). Based on experimental measurements of the covalent bond strength of the C-O bond (Grandbois et al, 1999), we have estimated the critical scission tension of the DNA chain. Typical DNA solutions contain chain samples with a wide distribution of chain sizes, thus the analysis of chain scission in contraction flow becomes difficult. In this study we have used lambda-DNA samples which have a uniform chain size to determine the critical tension for scission in contraction flow unambiguously. Our scission experiments and the critical scission tension are in quantitative agreement with the tension estimate from the C-O bond strength. To better understand this process we then use the Kramers bead-rod chain model to simulate DNA chains in contraction flow. Scission predictions from these simulations are in good quantitative agreement with the experiments. We present results in simple shear and extensional flow to better understand chain fragmentation mechanisms and then apply our understanding to the complicated mixed flow situation of contraction flow. We find parabolic tension profiles along the chain in extensional flow, resulting in mid-chain scission while in shear flow we find fluctuating tension profiles due to tumbling motion of the chain, thus resulting in random scission along the chain. The contraction flow is extensional along the symmetry line and shear along the wall of the contraction. Thus by controling the contraction flow geometry one can control the distribution of chain sizes.

Thursday 9:20 Ballroom D SM4

Effects of flow and confinement on DNA dynamics in microfluidic devices

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The dynamics of dissolved long-chain macromolecules are very different in highly confined environments, such as microfluidic devices, than in bulk solution. We present here a computational method for quantitatively predicting these dynamics, and apply it to the behavior of DNA in micron-scale flow channels. The method self-consistently combines a coarse-grained Langevin model of the polymer dynamics with a numerical solution for the flow generated by the motion of polymer segments. With the method, relaxation time and diffusivity are shown to depend strongly on confinement through hydrodynamic interactions, with a very broad crossover from free-solution behavior. We also examine mass distributions and chain stretch for flow through channels and slits. Finally, we study in detail the relaxation of a fully stretched chain in a channel, finding the striking result that chains move toward the channel walls as they relax -- a chain is convected toward the channel wall by the flow it generates while relaxing.

Thursday 10:10 Ballroom D SM5

Tracer microrheology of complex fluids and gels

Frédéric Cardinaux[1], Luca Cipelletti[2], Frank Scheffold[1], Peter Schurtenberger[1], Cornelia Heinemann[3], Felix Escher[3], and Béatrice Conde-Petit[3]
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We have studied the thermal motion of tracer particles embedded in strongly viscoelastic complex media by dynamic light scattering and classical oscillatory shear measurements. The first system we address is a concentrated aqueous solution of the surfactant $C_{16}E_6$. Under the chosen conditions (c = 100 mg/ml, 0.005 M KCl), long elongated (polymer like) micelles are formed, resulting in a strongly viscoelastic liquid. The motion of micron-sized tracer spheres dispersed in the system has been monitored using diffusing wave spectroscopy (DWS). From the measured single particle mean square displacement we obtain the loss and storage moduli, $G''(w)$ and $G'(w)$, using a generalized Stokes-Einstein relation (GSER). Moreover we present a combination of single and multi-speckle DWS offering an extended range of accessible timescales (and therefore frequencies w), typically from 10^{-8}s to 100s or more. The second system under study is a mixture of potato starch dispersion and flavor compounds. The interaction of these components is interesting from the point of view of binding and release of volatile flavors in food systems. Typically a rapid complexation induced gelation is observed, difficult to follow in detail using traditional techniques. We demonstrate that in a single tracer microrheology experiment, the full frequency dependent loss and storage moduli, $G''(w)$ and $G'(w)$ can be accessed with a time resolution of a minute or better. Starting from a simple fluid we observe after a few minutes the collapse of the elastic moduli to a single curve $G''(w) = G'(w) \sim w^{0.5}$, one of the hallmarks of critical gelation. With increasing waiting time the gelation process saturates (after about 60 min) and a weak biopolymer gel is formed. For both systems we find microrheology and classical rheometry in good agreement over the time and frequency range accessible to both techniques.

Thursday 10:35 Ballroom D SM6

Tracer Brownian motion in complex fluids

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The utility of tracer microrheology in probing the structure and dynamics of complex fluids is gaining increasing recognition. This is primarily due to the significant advantages that tracer microrheology provides over traditional mechanical rheometry such as gently probing a material?s linear response over a wide frequency range and small sample volumes. The underlying basis of the technique relies on having a correct understanding of the connection between the Brownian or thermal motion of the probe particles and the viscoelastic response of the suspending media. Although this connection has been well established for simple viscous fluids it is still not well understood for viscoelastic media. This to primarily due to:(i) the presence of local heterogeneities in these complex systems, (ii) the possible perturbation of the local rheological properties brought about by the probe particles and (iii) the influence of longitudinal dynamical modes. Previous experimental investigations have primarily focused on aqueous biopolymer solutions where the above mentioned factors do not seem to play a significant role. Recent investigations indicate that the above-mentioned factors may significantly influence tracer Brownian motion. In order to gain a deeper understanding of the connection between the probe Brownian motion and the viscoelastic response of the suspending media, comprehensive studies of several polymer and surfactant solutions-semi-dilute PEO solutions, CTAB/KBr & CTAB/NaSal wormlike micelle solutions, PluronicTM F108 micellar dispersions & FCC soft crystals-were undertaken. Tracer microrheology results are reported for both ensemble diffusing wave spectroscopy-based ensemble and one & two particle tracking measurements. In addition, the tracer microrheology and mechanical rheometry experiments are complimented with dynamic & static light scattering and small angle x-ray scattering (SAXS) studies in an attempt to sort out the various phenomena influencing tracer Brownian motion in complex fluids.

Thursday 11:00 Ballroom D SM7

Two-point microrheology and rearrangement noise in living cells

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A major goal of developing microrheological methods is to understand how a living cell creates and regulates its unique mechanical properties. We report direct microrheological measurements of the stochastic fluctuations of the cytoskeleton of living animal cells as a function of spatial and temporal frequency. The observed strain fluctuations are three orders of magnitude larger than expected from thermal processes, and are likely due to motor-driven cytoskeletal rearrangements. The noise is found to be spatially white, and to have a roughly 1/f temporal power spectrum. This observation provides direct support for, and is naturally explained by the recently proposed Soft-Glassy-Rheology (SGR) model of cytoskeletal mechanics, recently put forward by Fabry et al.

Thursday 11:25 Ballroom D SM8

Matrix fluorescence photobleaching recovery - a diffusion based method for determining polydispersity

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Fluorescence photobleaching recovery (FPR) is a classic method for measuring diffusion. FPR was developed for biological systems, but has been adapted to study polymer diffusion in complex fluids. An attribute of the technique is the ability to measure diffusion coefficients of dilute probe polymers in the presence of concentrated matrix polymers. The matrix increases the dependence of the probe diffusion coefficient on probe molar mass. Such "stretching" of the relationship between D and M makes it easier to resolve mixtures of diffusing polymers. Just as gel permeation chromatography identifies molar masses by elution volume, matrix FPR can identify masses by diffusion coefficient. Both methods require calibration, but the amount of material required for calibration is minute for FPR, simplifying calibrations with precisely the same polymer to be analyzed. There is no physical separation of the analyte in matrix FPR, but sample volumes are small, and the instrument can switch quickly between conditions of temperature, salt, or pH. Simulations of FPR data based on the deGennes reptation model, which predicts that D scales inversely as the square of molar mass, suggest that matrix FPR can provide adequate polydispersity determinations in realistic cases. This is especially true of commercial water solubles, which are easily labeled. A probe diffusion experiment of fluorescein isothiocyanate labeled dextrans or 5-(4,6-dicholorotriazinyl)aminofluorescein labeled pullulans diffusing through an unlabeled, high molar mass dextran at concentrations of 5-25% w/w was used to test this hypothesis. Useful separations were obtained, although D scaled much more weakly than the deGennes expectation in the chosen systems. This is apparently due to the lack of entanglements as confirmed by the absence of an identifiable plateau modulus. This work supported by the National Science Foundation, Division of Materials Research.

Thursday 11:50 Ballroom D SM9

Linear elasticity of cubic phases in block copolymer melts by self consistent field theory

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We examine the static linear elasticity of the cubic phases of diblock copolymer melts using self-consistent field theory. We calculate the SCF free energy of affinely deformed crystal strucutres from which we extract linear elastic moduli for the bcc and gyroid phases. The calculated elastic moduli compare well with experimental measurements of the low frequency plateau value of the storage modulus

We also test the ability of a model of soft spheres interacting via a pair potential to explain the elastic behavior of a bcc crystal. We calculate the SCF elastic response for both fcc and bcc micellar crystals and compare to predictions of the elastic modulus based on a nearest neighbor pair potential. We find that the calculated linear elastic behavior of bcc and fcc crystals is inconsistent with the pair potential hypothesis.

Poster Session

Organizer: Eric M. Furst

Wednesday 6:00 Humphrey Room PO1

Rheo-optical investigations on polymer-clay nanocomposites

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The shear orientation of viscoelastic polymer-clay nanocomposites in bulk and in solution was investigated by means of rheology and flow-birefringence. The polymer chains are in dynamic adsorption/desorption equilibrium with the clay particles to form a "network". The elastic behavior of the network was characterized by constant stress, oscillatory shear and stress relaxation experiments. Experiments under steady flow characterized the transient behavior of the network. The orientational alignment of the platelets inside the network is a competition between i) flow alignment and ii) orientational and configurational relaxation. Flow alignment is induced by orientation of platelets and stretching of polymer chains under shear. Orientational and configurational relaxation is caused by a randomization through adsorption/desorption processes at clay surfaces. Increasing adsorption times of the polymer attached to the clay drive the equilibrium towards i) while desorption favors ii).

Wednesday 6:00 Humphrey Room PO2

Nonlinear dynamics of a concentrated system of rigid rods subjected to periodic shear flows

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The peculiar behaviour of nematic liquid crystalline phases has been widely addressed in the recent literature. Under steady shear flows, and in homogeneous conditions, different regimes have been theoretically predicted, and in some cases experimentally observed. In particular, periodic and even aperiodic regimes have been detected. Some of the observed peculiarities can be reexamined within the framework of the group theory. Moreover, the natural oscillating behaviour, as the well known tumbling or wagging regimes, can give rise to a number of resonance phenomena when the system is forced with proper periodic flows. For example, frequency locking phenomena are predicted by modelling the nematic system with the rigid rod model.

Wednesday 6:00 Humphrey Room PO3

Controlling gelation in polymer-clay dispersions

Heidi Sardinha and Surita R. Bhatia
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We present rheological data on two model clay-polymer systems, aqueous dispersions of laponite XLG and laponite RD with added polyethylene oxide (PEO), which is known to adsorb on the clay surfaces. We find that added PEO significantly slows down gelation and decreases the complex viscosity and elastic modulus of the dispersion by several orders of magnitude. These effects are more pronounced for higher polymer concentrations and molecular weights. These counterintuitive results are somewhat surprising in light of recent work by Han and co-workers that show increased elasticity and viscosity for laponite in the presence of PEO due to formation of a transient network. We believe that our PEO chains are too short to form interparticle bridges and thus cannot form an associative network between clay particles. However, the adsorbed PEO layers may provide a steric barrier to electrostatic aggregation of clay particles, thus preventing or slowing gel formation. These results can potentially impact the formulation of coatings, adhesives, and cosmetics.

Wednesday 6:00 Humphrey Room PO4

Dynamic simulation of bidisperse magnetorheological fluids

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Particle level simulations are employed to investigate the rheological properties of bidisperse magnetorheological (MR) fluids. These particulate suspensions are treated as nonlinearly magnetizable, neutrally buoyant, non-Brownian spheres immersed in a nonmagnetic, Newtonian continuous phase. The evolution of the suspension microstructure is described by Newton's equations of motion, including interparticle magnetostatic forces, hydrodynamic forces and short-range repulsive forces. The magnetostatic forces are treated in the point-dipole limit, and include non-linear magnetization and a self-consistent approximation to multibody interactions. Various properties of the suspensions are investigated, including such rheological properties as the yield stress and the linear viscoelastic response, as well as the effective suspension permeability. Simulations show that the dynamic yield stress of bidisperse suspensions is larger than that of monodisperse suspensions at the same particle volume fraction. In this presentation we will examine effect of the particle size distribution, volume fraction and field strength on the yield stress and the effective permeability. We will also discuss the connection between the suspension structure and the enhanced rheological response for bidisperse suspensions.

Wednesday 6:00 Humphrey Room PO5

Shear-induced self-diffusivities of a dilute suspension of rough spheres in nonlinear shear flow

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Experimental investigation by Eckstein et al. (1977), showed that $D = 0.025\,\dot{\gamma}\,a^2$ at moderate concentrations, where a is the particle radius, $\dot{\gamma}$ is the shear rate of the flow, and D is the self-diffusivity. Leighton & Acrivos (1987) in more recent experiments have shown $D = 0.5\,c^2\dot{\gamma}\,a^2$ for $0.05 < c < 0.4$ where c is the particle concentration.

When two spheres interact in a shear flow, the minimum separation cannot be less than their surface roughness, which will cause the trajectories of spheres irreversible. In simple shear flow, da Cunha & Hinch (1996) found that $D = c\,\dot{\gamma}\,a^2 f$, where f is a function of particle surface roughness e.

In this work, the shear-induced self-diffusivities of a dilute suspension of rough spheres in nonlinear shear flows were numerically obtained by using a three-dimensional boundary element method, in which the effect of surface roughness is included by preventing the minimum separation of the two spheres to be less than ea in both linear and non-linear shear fields. It is found that our numerical results are in general agreement with those of da Cunha & Hinch in simple shear flow, which showed that D is constant everywhere for a specific surface roughness and particle concentration. However, in a plane Poiseuille flow, our results show that $D = c\,\dot{\gamma}_{12}\,a^2 f$, where $\dot{\gamma}_{12}$ is the shear rate at the center-of-gravity of the two-sphere system which is a linear function of the location, indicating that D is a linear function of the location. Our results also show that f has the same value both in the simple shear and plane Poiseuille flow for a specific surface roughness and particle concentration and there is no effect of the characteristic length of plane Poiseuille flow on f.

Wednesday 6:00 Humphrey Room PO6

Surface morphology of drying latex films

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When a drop of aqueous solution containing suspended particles dries, particles accumulate at the contact line. Often the contactline undergoes a sequence of pinning-depinning events with particles accumulating whenever the contact line is pinned. These processes lead to ring formation, the details of which are examined here. In particular, we provide detailed measurements of ring formation as a function of the drop radius and the size of the suspended

particles, and we report measurements of the time-dependence of the essentially stochastic pinning-depinning cycles of the contact line motion.

Wednesday 6:00 Humphrey Room PO7

Three dimensional boundary element simulations of concentrated suspensions in a spinning ball rheometer

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The spinning ball rheometer has been proposed as a method to measure rheological properties of concentrated suspensions. Recent experiments have shown that the measured extra torque on the spinning ball decreases as the radius of the spinning ball becomes comparable to the size of the suspended particle. We have performed a series of three dimensional boundary element calculations of the rheometer geometry to probe the microstructure effects that contribute to the apparent 'slip.' We will present a series of snap-shot results as well as several transient calculations which are compared to the available experimental data. The computational limitations of these large-scale simulations shall also be discussed.

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Wednesday 6:00 Humphrey Room PO8

Rheological properties and interfacial tension of polypropylene-poly(styrene-co-acrylonitrile) blend containing compatibilizer

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Rheological and morphological properties of the polypropylene (PP) and poly (styrene-co-acrylonitrile) (SAN) blend containing polypropylene-g-poly(styrene-co-acrylonitrile) (PP-g-SAN) was studied by advanced rheometric expansion system (ARES) and scanning electron microscopy (SEM). In the study of the complex viscosity of the PP-SAN (20/80) blend, the complex viscosity of the blend showed maxaimum value in the 1.0 phr PP-g-SAN copolymer content, which suggested that the compatibilizing effect of the PP-g-SAN copolymer was achieved. From the morphological studies, the PP-SAN (20/80) blend showed droplet dispersion type morphology, and the PP droplet size showed minimum value in the 1.0 phr PP-g-SAN copolymer content. The interfacial tension of the PP-SAN (20/80) blend was determined from the morphological studies and form relaxation time using the Palierne and the Choi and Schowalter models and showed minimum value in the 1.0 phr PP-g-SAN copolymer content in each models. From the results of the morphological, rheological studies and the values of the interfacial tension, it is suggested that the compatibility of the PP-SAN (20/80) blend increases more in the 1.0 phr PP-g-SAN copolymer content.

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Wednesday 6:00 Humphrey Room PO9

Effects of pressure and supercritical CO_2 on the rheological properties of polymer melts

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Supercritical carbon dioxide (SC-CO_2) has been used as a physical blowing agent in the plastic foaming process and as a plasticizer to reduce melt viscosity in melt processing. However, there has existed no accurate method to measure the rheological properties of molten plastics containing CO_2 under typical processing pressures. A high-

pressure sliding plate rheometer developed at McGill University was modified to carry out experiments with SC-CO_2 at elevated pressures. This rheometer can generate controlled, homogeneous shearing deformations at a uniform pressure in either strain- or stress-control modes. Edge effects are not a problem, as the shear stress is measured in the center of the sample using a shear stress transducer.

A technique to measure the effect of dissolved SC-CO_2 on the rheological properties of molten polymers is described, and experimental data showing the effects of pressure and CO_2 on the viscosity and creep compliance are presented.

Wednesday 6:00 Humphrey Room PO10

A constant volume model for immiscible polymer blends

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We present a set of time evolution equations describing the effects of a general deformation field on the shape, size, and orientation of constant volume droplets suspended in a Newtonian fluid. The viscometric functions of this incompressible and immiscible polymer blend are derived together with the above mentioned set of equations. For the constant volume constraint we adopt a relationship due to Almusallam et al. (2000) which is implemented using a recent methodology of Edwards et al. (2002). The morphological and viscometric features of the model are evaluated and discussed for step strain and shear relaxation profiles.

A. S. Almusallam, R. G. Larson, M. J. Solomon (2000) A constitutive model for the prediction of ellipsoidal droplet shapes and stresses in immiscible blends. *J. Rheol.* 44, 1055-1083; B. J. Edwards, M. Dressler, M. Grmela, A. Ait-Kadi (2002) Rheological models with microstructural constraints. *Rheol. Acta*, in press.

Wednesday 6:00 Humphrey Room PO11

Electromagnet for magnetorheological testing of solid and liquid magnetic suspensions

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An electromagnet has been designed and tested to extend magnetorheological (MR) capabilities of the AR 1000 Rheometer from TA Instruments. The design, which is based on the Helmholtz Coils configuration, provides a uniform field in a large volume, and allows easy access to the sample. The electromagnet is capable of producing magnetic fields of at least 1.5 T within 5 mm gap between the magnet core poles. The gap between the coils in the magnet can be adjusted to accommodate various attachments for rheological testing and different types of samples. The device allows one to measure the normal stress in MR samples, and can also be used in rheological tests that require the cone-plate or concentric cylinder configuration. An air-cooling system is built into the electromagnet coils, but it can be modified to be used with water or any other liquid. A major advantage of the magnet design is its flexibility.

Results from testing liquid and solid MR suspensions demonstrate capabilities of the magnet design. Using a parallel plate configuration, the shear modulus of a liquid MR suspension in various magnetic fields, and the redistribution of magnetizable inclusions due to shear flow in the presence of a magnetic field are measured. The elastic modulus of solid MR composites is measured with a torsion test under various magnetic field strengths.

Wednesday 6:00 Humphrey Room PO12

Dynamic model for breakup of agglomerates in polymer melts under shear and extensional flows

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A dynamic predictive model of agglomerates deformation and breakup in viscous fluids is developed by taking into consideration the hydrodynamic forces and the particle-particle interaction forces which induce flocculation and yield stresses in suspensions. An agglomerate in a polymer melt compound is represented as an assembly of small spherical particle elements. During the mixing of fillers in polymer melts, agglomerates are dispersed and distributed

in the matrix depending on the local stress fields in the fluids. This deformation and breakup process of coagulated particles is numerically investigated by using the Discrete Element Method (DEM). The proposed DEM model is applied to simulate the deformation and breakup process of particle-agglomerates under shear flows. The simulation model we have developed describes the deformation and the breakup phenomena of agglomerates in the flow fields adequately. It is also indicated that the coalescence of particles occurs during the dispersion process. The average number of particles in broken fragments is related with the intensity of flow field. It is found that the agglomerate becomes smaller as the shear stress in the flow field increases.

Wednesday 6:00 Humphrey Room PO13

Dynamic properties of shear thickening colloidal suspensions

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Shear flow-jamming or shear thickening in colloidal dispersions is characterized by the abrupt transition from liquid to solid as the applied shear stress is increased. Experiments are performed on model, electrostatically stabilized colloidal suspensions to compare the shear thickening behavior under steady and dynamic oscillatory flow. Reversible shear thickening is observed and the transition stress compares well to theoretical predictions. Steady and transient shear thickening are observed to occur at the same value of the average stress. The critical strain for shear thickening is found to depend inversely on the frequency at fixed applied stress for low frequencies (high strains), but tends to a minimum critical strain at higher frequencies. Lissajous plots illustrate the transition in material properties through the shear thickening transition, and the energy dissipated by a shear thickening suspension is analyzed as a function of strain amplitude. Measurements of shear slip in the shear thickened state show that the existence of a minimum critical strain for shear thickening at high frequencies is a consequence of slip. Numerous data sets in the literature can be understood within the context of these measurements.

Wednesday 6:00 Humphrey Room PO14

Determining end-effects in concentrated suspensions of neutrally buoyant particles

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Experiments were performed to explore the axial end effects in concentrated suspensions as determined by a small ball falling along the axis to the bottom of the containing cylinder. The neutrally buoyant suspensions were composed of mono-dispersed polymethyl methacrylate spheres ranging in diameter from 0.1 mm to 6.35 mm in a refractive-index -matched viscous Newtonian fluid, with the volume concentration of solids, Φ , ranging from 10% to 50%. The experimental conditions were such that only hydrodynamic forces exerted an appreciable effect on the particles. Balls of various radii, a, were dropped along the centerline of cylinders whose radii, R, were 25.4 mm and 36.2 mm.

In a pure Newtonian fluid, the small falling balls begin to slow down appreciably from their steady state velocity at approximately one containing cylinder radius from the bottom of the container. The results of these experiments show that suspensions sense boundaries over much greater distances than pure Newtonian fluids and that these end effects increase dramatically as a/R and Φ increase. For example, when $a/R = 0.106$ in suspensions in which $\Phi = 50\%$, significant end-effects are measurable at about eight cylinder radii from the bottom of the cylinder.

Wednesday 6:00 Humphrey Room PO15

Rheological control by reversible flocculation

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The rheology of concentrated dispersions of sub micron inorganic particles is controlled by controlling the degree of reversible flocculation of the particles. The particles are dispersed using a surfactant combination in a mixture of water and propylene glycol. The yield point and viscosity were both found to increase as the proportion of propylene glycol in the continuous phase increased.

A model is proposed to explain the observed behaviour that is presently under investigation. As the hydrophobicity of the continuous phase is increased by increasing the proportion of propylene glycol the surfactant partitions away from the particle surface causing the particles to interact more strongly.

Wednesday 6:00 Humphrey Room PO16

Visualization of single DNA-single obstacle collisions

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Understanding polyelectrolyte-obstacle collisions is crucial in order to improve DNA electrophoretic separations in microfluidic devices containing rigid obstacles (Doyle et. al. *Science* 295 (2237), 2002). We present data from the observation of single DNA molecules in electrophoretic motion colliding with single microfabricated obstacles. The obstacle-filled microchannels (1.5 um columns in a 50 um wide by 2 um high channel) are fabricated out of PDMS using soft lithography. Large DNA fragments (48.5-168.9 kbp) are fluorescently dyed with TOTO-1 for microscopic observation. The time evolution of the center of mass velocity is followed under a microscope and tracked using custom software routines to quantitatively analyze the collision process. This data leads to a distribution of unhooking times for each size DNA molecule at a given electric field strength and shows the importance of molecular elasticity in providing separation of DNA. The data from strong electric field collisions are compared to previous simulations. Furthermore, the collision data provides unique insight into the molecular dispersion of the DNA separation device.

Wednesday 6:00 Humphrey Room PO17

Reptation dynamics in mixtures of long and short chains: Tube dilation and impeded curvilinear diffusion

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This theoretical and experimental investigation of reptation dynamics in binary mixtures of entangled short and long chains of the same species, inspired and verified by the experimental observations, proposes a new reptation theory to account for (a) the tube dilation (TD), (b) impedance of the long chain' curvilinear diffusion and (c) enhanced contour length fluctuation, all due to the incorporation of the short chains of length N_S. Our experimental data indicate that the TD suppresses the terminal plateau modulus according to $G_{pl}(\phi) = G_0[a/a_L(\phi)]^2$, where G_0 is the plateau modulus of a monodisperse melt and (a_L/a) is the tube dilation factor, corresponding to the enlargement of the tube diameter from a to a_L. The short chain's impedance on the long chain's curvilinear diffusion, characterized by an impedance function λ that explicitly depends on ϕ and N_S,is evident from the comparison between the theory and experiment. Finally, the contour length fluctuation (CLF) is found to play a subtle role in governing the concentration dependence of the terminal relaxation time: the correction due to CLF is larger at lower concentrations and for lower molecular weights of the long chains.

Wednesday 6:00 Humphrey Room PO18

Temperature and composition dependence of monomeric friction factors in a miscible polymer blend obtained by rheology and diffusion

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The composition and temperature dependence of the monomeric friction factor of each component in a miscible polymer blend is currently a subject of interest. The longest relaxation times of each component in the model miscible blend system of 1,2-polybutadiene and 1,4-polyisoprene have been examined as a function of temperature and composition. The longest relaxation time of each component provides an estimate of the monomeric friction factor via an empirically modified reptation equation. This friction factor is in good agreement with values estimated from tracer diffusion measurements. The composition dependence of the monomeric friction factor of each component in the blend appears to be well described by a composition dependent effective glass transition temperature. In addition, the frequency dependence of the storage and loss moduli of the miscible blend in the linear viscoelastic regime is well described by the entanglement model of Tsenoglou.

Wednesday 6:00 Humphrey Room PO19

Filament depletion from colloidal probe particles in F-actin networks

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Tracer particle microrheology enables one to determine the viscoelasticity of materials by measuring the thermally-driven motion of embedded probe particles. Because of its large frequency range (0.1-10^6 Hz), minimal perturbation, and sensitivity to local response, including heterogeneity, microrheology is becoming increasingly important for probing the rheological properties of individual cells and cytoskeletal biopolymers. However, such measurements depend strongly on the interaction between the probes and the suspending medium, and can be altered by changing the tracer particle surface chemistry. Here we present the role of particle surface properties on measurements of the high-frequency viscoelastic shear modulus for networks of filamentous actin, a principle component of the cytoskeleton. Using diffusing wave spectroscopy to measure tracer motion, we find that protein-coating leads to substantially less sensitivity to the actin network, resulting in a lower apparent shear modulus amplitude and higher phase angle. Our results indicate that polymer depletion around tracer particles occurs under conditions where the filaments are not physically bound to the particles.

Wednesday 6:00 Humphrey Room PO20

Rheology measurements of thin polymer films using the atomic force microscope

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Results of tan delta measurements of thin polymer samples (thickness < 0.13 mm) will be presented. For the AFM measurements, a thin polymer sample was oscillated sinusiodally by a piezo transducer at amplitudes below 0.125 microns. A 25-micron glass sphere that was attached to an AFM cantilever was brought into contact with the oscillating polymer sample. The the amplitude and phase shift response of the AFM cantilever (as measured by the photodiode signal) were used to calculate the tan delta of the polymer material as a function of the measured oscillatory frequency (0.01 to 100 Hz). The results show excellent quantitative agreement to Rheometric Data Analyzer (RDA) measurements of polymer films 20 times thicker.

Wednesday 6:00 Humphrey Room PO21

The dependence of the viscosity of semiflexible chains on the chain contour length, polymer concentration and persistence length

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The dependence of the (linear) viscosity h on the chain contour length L, the persistence length a, and the polymer concentration c in solution is analyzed for solutions of several linear semiflexible chains. Data from the literature on polymers over a wide range in a are examined, using a semiempirical representation for h expressing the crossover from dilute to concentrated solution behavior (e.g., see *J. Rheol.* 1996 40: 1129-54). In this representation, it is found that for a wide range of flexible chain polymers, the crossover to viscous behavior dominated by entanglement effects occurs when a reduced parameter X, proportional to the concentration multiplied by the mean-square radius of gyration at that concentration, is about equal to 100 for many polymers. The analysis shows that although the semiempirical relation can be applied to represent the behavior of h on L and c, the critical value of X so determined for some semiflexible chains can be decreased substantially below its normal value of about 100. However, this decrease does not seem to correlate with a in any apparent way, indicating that some as yet unidentified molecular characteristic may be involved in the viscous behavior. It is suggested that this may be an intrinsic dynamic rigidity of the chain conformation, not measured in the equilibrium persistence length a.

Wednesday 6:00 Humphrey Room PO22

Modifying the rheological properties of collagen-rich tissues by crosslinking

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Non-enzymatic crosslinking causes a variety of collagen-rich tissues to lose their elasticity with age (e.g., hardening of arteries and wrinkling of skin). We examine the effects of crosslinking on the viscoelastic properties of tissue using glyceraldehyde as a model crosslinking agent and the cornea as a model tissue. The nanostructure of the material is reminiscent of a hexagonal-ordered phase in block copolymers, with the cylinders largely composed of collagen fibrils and the continuous phase consisting of proteoglycan hydrogel. Rabbit and human corneas are treated under culture conditions that maintain normal morphology and hydration of the cornea. Glyceraldehyde is applied topically (drops of 3% wt. glyceraldehyde in saline are applied 3 times a day for six days) and the shear modulus is characterized subsequently using a parallel plate geometry. Substantial increases in the shear modulus are observed: 3 fold in rabbit and 5 fold in human corneas. Studies of model collagen systems---collagen fibrils from rat-tail tendon and reconstituted collagen gels---indicate that interfibrillar cross-linking is responsible for the change in the mechanical properties of corneas. Analytical biochemistry is used to identify the molecular structure of chemical crosslinks, which form predominantly between the primary amines of lysine residues.

Wednesday 6:00 Humphrey Room PO23

Block copolymer micellar soft crystal dynamics and structure

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A comprehensive tracer microrheology/mechanical rheometry study of aqueous FCC crystal forming triblock copolymer PluronicTM F108 solutions is described. Experiments were carried out over a wide concentration range wherein the solution microstructure varied from an isotropic micellar dispersion to a soft FCC polycrystal. The tracer microrheology and mechanical rheology experiments are complimented with static light scattering and small angle x-ray scattering (SAXS) studies, which provide direct information on the micellar dispersion static structural properties. The micellar dispersion osmotic pressure concentration dependence is determined from the static light scattering measurements in order to ascertain the potential influence of osmotic compressibility on tracer Brownian motion and to probe the nature of the intermicellar interactions. In addition to exploring the possible effects of longitudinal dynamic modes on tracer Brownian motion, another focus of the study is the high frequency FCC soft crystal dynamics. Diffusing wave spectroscopy-based tracer microrheology measurements provide access to very high frequencies. This high frequency dynamical information when combined with the micelle radial distribution function determined from SAXS measurements provides additional insight into the micellar interactions that underlie the behavior exhibited by these industrially important surfactant systems.

Wednesday 6:00 Humphrey Room PO24

Shear-induced structure and dynamics of a hydrophobically modified polymer in the presence of anionic surfactant

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The complex flow behaviour resulting from the addition of varying concentrations of an anionic surfactant sodium dodecyl sulphate (SDS) to a semi-dilute solution of 0.5 wt% hydrophobically modified hydroxyethyl cellulose (hmHEC) solution has been investigated utilising rheometry and dynamic and static light scattering. Both dynamic and steady shear behaviour of this polymer-surfactant complex have been examined, showing that between SDS concentrations of 0.2 and 0.25 wt%, the shear viscosity of the hmHEC-SDS complex network undergoes shear-induced thickening, followed by a two-stage shear-induced fracture or break-up of the network. At high applied stress, a partial, local break-up of the network occurs, while at still higher stress, above the critical or network yield stress, a complete fracture of the network into small microgel-like units is believed to be invoked. This second network rupture is progressive with time of shear and no steady state in viscosity was observed even after 300 s. The structure which was reformed after the cessation of shear is observed to be different from the original equilibrium state. Rheological properties are combined with results from light scattering to provide a mechanistic model for the shear induced structure within these complex systems.

Wednesday 6:00 Humphrey Room PO25

The structurization and rheology of diblock copolymer/hydrocarbon solutions

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The phase behavior and rheology of squalane solutions of a diblock copolymer, hydrogenated polystyrene-block-polyisoprene (SEP, Kraton G1702), were studied over a wide range of temperatures and concentrations (0.5 to 10 wt.%). Micellar solutions with blue tinge were formed at low concentrations. The blue tinge disappeared when the solutions were heated to about 150 °C, signifying the dissolution of micelles, according to the studies of Watanabe and Hashimoto [1,2], among others. Although no additional phase transformations were observed up to 200 °C, anomalous temperature-rheological behavior in the 5 and 10 wt.% solutions was found. Dynamic temperature/frequency sweeps showed that the solutions behaved like solids at very low temperatures ($T < -50$ °C). Upon increasing the temperature, the solutions melted into viscous liquids with terminal flow behavior at low frequency. Then, at about 40 °C and 70 °C for the 5 % and 10 wt.% solutions, respectively, the storage modulus began to increase abruptly and rose almost one decade within a temperature range of 20 °C and exceeded the loss modulus. At yet higher temperatures, dynamic frequency sweeps demonstrated that the solutions exhibited gel-like behavior. The gel structure didn't melt in both solutions even at temperatures as high as 200 °C. A large hysteresis was observed; the solutions did not recover to their liquid-like rheological behavior in the cooling process, but did recover their original properties at low temperatures. The kinetics of gelation from 30 to 150 °C in the 10 wt.% solution appeared to follow the Arrhenius relationship with an activation energy of 37 kJ/mole.

Reference: [1] Hiroshi Wantanabe and Tadao Kodaka, *Journal of Rheology*, 1982, 26 (2), 153-179. [2] Takeji Hashimoto, Mitsuhiro Shibayama and Hiromichi Kawai, *Macromolecules*, 1983, 16(1), 16-28.

Wednesday 6:00 Humphrey Room PO26

Design, synthesis, and thermomechanical characterization of a new triblock copolymer with shape memory effects

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Polymers that have a shape memory effect are increasingly attracting the attention from polymer scientists and engineers recently. Compared with classical shape memory alloys (SMA), shape memory polymers (SMP) feature distinct advantages of: (i) recoverable strain can be extended to several hundred percent compared with less than 8% for SMA. (ii) tuning of transition temperatures and the mechanical energy stored by varying the composition of the polymers or the processing, and (iii) significantly lower cost and ease of processing compared with SMAs. In our lab, we have designed and synthesized a new type of shape memory polymer in the form of an ABA triblock copolymer with two different monomers, each biodegradable. The central section of the polymers is semicrystalline and its melting temperature can be used as the critical temperature for triggered strain recovery and this temperature can be tuned by controlling the block length. The end sections of the block copolymer provide physical crosslinking, being themselves semi-crystalline, but with a melting point 100 ºC above that of the central block, B. Below the transition temperature of block B, the polymers are rigid with a tensile modulus near 3 GPa, as both blocks are highly crystalline and feature Tg's above room temperature. When the polymers are heated above the melting point of block B but below that of A, the polymers behave in a rubbery manner with the modulus plateau determined by the physical crosslink density (volume per A-domains) and the entanglement density of B. This new polymer can be extruded or molded by heating the polymer above the melting points of both section A and B, unlike most SMPs that require chemical crosslinking. We will present the synthesis and the thermo-mechanical characterization of the mew materials with an emphasis on thermally stimulated strain recovery; i.e., shape memory.

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Wednesday 6:00 Humphrey Room PO27

Linear viscoelastic behavior of a polymeric bicontinuous microemulsion

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Ternary polymer blends comprising two homopolymers and their corresponding symmetric diblock copolymer self-assemble into a bicontinuous microemulsion, analogous to oil/water/surfactants. The slower dynamics of polymeric systems facilitates the study of rheological properties of this morphology. In the present study, the equilibrium viscoelastic behavior of a model polymeric bicontinuous microemulsion is investigated, and comparisons are made with the predictions of a time dependent Landau-Ginzburg model. The microemulsion consists of a ternary blend of poly(ethyl ethylene) (PEE), poly(dimethyl siloxane) (PDMS) and a symmetric PEE-PDMS diblock copolymer. Dynamic mechanical spectroscopy within the linear viscoelastic regime reveals a response remarkably similar to that of diblock copolymer lamellar phases just above the order-disorder transition. The data can be fit to a generalized Maxwell model; the "excess" viscoelastic contribution from the microemulsion structure is extracted by subtracting out the background contribution from the pure components. The experimental data are compared with the predictions of the Landau-Ginzburg model of Patzold and Dawson. Complementary small angle neutron scattering experiments give the structural parameters of the microemulsion, and dynamic light scattering provides the Onsager coefficient, which are used as inputs for the model. The essential features of the viscoelastic behavior are captured; however there is significant failure in obeying both the magnitude and the temperature dependence of the zero shear viscosity and the average relaxation time.

Wednesday 6:00 Humphrey Room PO28

Double reptation predictions of linear viscoelasticity in miscible polymer blends

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We present results of a numerical calculation of the linear viscoelastic complex modulus of model miscible blends of poly(isoprene) and poly(vinyl ethylene). An average-longest segmental relaxation time is calculated for both components from the segmental relaxation time distribution, generated by an improved model for segmental dynamics in miscible blends, which treats both intra-molecular effects (due to chain connectivity) and inter-molecular effects (arising from blend thermodynamics). This average-longest segmental time is treated as the monomer relaxation time of the tube model, with which the terminal relaxation time of each component is calculated. The component terminal relaxation times and the plateau modulus of the blend are input to the double reptation model (des Cloizeaux form). The calculated modulus is seen to be in reasonable qualitative agreement with experimental data. Thermorheological complexity, seen experimentally in PI/PVE blends, is also predicted.

Wednesday 6:00 Humphrey Room PO29

Multiscale theory and simulation of rheological properties in sheared mesophase pitches

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Mesophase pitches are multicomponent discotic nematic liquid crystals, whose characteristic molecular weight is intermediate to low molar mass and polymeric nematic liquid crystals. Mesophase fluids are used in the aerospace, transportation and electronic industries. Flow modelling of these fluids is performed using a Landau-de Gennes model that takes into account short range and long range energy and flow-induced orientation. This mesoscopic viscoelastic model has been adapted to describe the rheology of flow-aligning thermotropic discotic nematic liquid crystals as models of mesophase pitches.

We develop a fundamental understanding of the relations between rheology and flow of carbonaceous mesophases using theory and simulation by characterizing the steady and transient shear rheological material functions of flow-aligning discotic nematic liquid crystals.

The simulations are able to capture the salient transient and steady rheological material functions. The predicted first normal stress difference, apparent shear viscosity and shear stress of discotic mesophases are consistent with the experimental data (A. Cato and D. Edie, Carbon Conference Proceedings, 2001, Paper 19.2). Our model captures all the observed features associated with the evolution of apparent shear viscosity for a wide range of shear rates, the first normal stress difference during shear flow with given constant low shear rate, and of the shear stress during shear start-up.

Wednesday 6:00 Humphrey Room PO30

Orientation behavior of a pentablock copolymer through solution extrusion

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The orientation behavior of polystyrene (PS) - polybutadiene (PB) pentablock copolymer (SBSBS, Mw = 105,000 g/mol, fraction of PB = 30 wt %) through a solution extrusion process was examined. The pentablock copolymer was dissolved in mixtures of toluene (a neutral solvent for each block) and heptane (a good solvent for PB). As for the solution state, the lamellar phase was accessible through the selective swelling effect of heptane on PB. The oriented lamellar structure of SBSBS was obtained after extrusion and solidification. It was revealed that the solvent composition, solidification method, slit geometry, and shear rate affect the orientation behavior of SBSBS. Interestingly, a transition of the orientation direction was observed with increasing shear rate, from perpendicular at low shear rate to transverse under high shear rate conditions. The orientation behavior of SBS triblock copolymer (104,000 g/mol, fraction of PB = 30 wt %) was also investigated in this study. Through the comparison of the orientation behavior between SBSBS and SBS, it is clear that the transverse lamellar orientation at high shear rates results from the unique architecture of the pentablock copolymer, i.e., the existence of bridging and looping blocks (i.e., the absence of slip planes). The transition from the oriented lamellae of SBSBS to oriented hexagonal cylinders through annealing will be also discussed.

Wednesday 6:00 Humphrey Room PO31

Birefringence as a probe to follow phase transitions

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Phase behaviour of a polyisoprene-polystyrene (PI-PS) diblock copolymer (of composition f PI =0.67) was studied by birefringence and rheology. This composition had been previously characterized by different researchers using SAXS, SANS and TEM and shown to form a lamellae, a metastable phase, gyroid and cylindrical phases at various temperature ranges. In this study, PI-PS was subjected low amplitude oscillatory shear during a temperature ramp in a rheometer (RSA II). In situ birefringence measurements were made where laser light was sent along the velocity gradient axes. Along with the shear modulus (G'), birefringence measurements confirm the formation of at least 3 stable phases and indicate formation of a metastable phase between lamellae and gyroid phases. Some of the phase transitions are observed as minor changes in G', while the same transitions gave a significant response in birefringence.

Wednesday 6:00 Humphrey Room PO32

Rheology of supercritical CO_2 plasticized acrylic copolymers

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Acrylonitrile copolymers are traditionally solution spun, using polar organic solvents such as DMF and DMAC, to avoid a degradation process that renders the copolymer intractable at melt processing temperatures. Carbon dioxide provides an environmentally benign plasticizer to replace traditional organic solvents used in the solution spinning of carbon fiber precursors. Supercritical carbon dioxide is used as a processing aid to plasticize similar high acrylonitrile content copolymers. Significant reductions in the glass transition temperature, up to 25°C, have been obtained. Pressurized capillary rheometry has shown up to 50 percent viscosity reduction in 90 percent acrylonitrile materials. Entry pressure and compressibility are considered to determine the effects of the applied static pressure and of the adsorbed CO_2. A WLF analysis predicts processing temperature reductions up to 20°C, which would slow the kinetics of degradation sufficiently to permit melt spinning of these materials.

Wednesday 6:00 Humphrey Room PO34

Shear rheology of fluoropolymers in the melt and solution states

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Wednesday 6:00 Humphrey Room PO35

Nonlinear rheology of entangled star polymers

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Entangled star polymers show significant differences from their linear counterparts in the linear viscoelastic regime, as the branch point of the star greatly inhibits reptation dynamics. Two-color flow birefringence experiments over a range of shear rates will be used to make comparisons between the response of 4-arm star and linear polybutadiene polymers in steady and transient shear flows. With extremely long relaxation times, stars provide an ideal platform for exploring relaxation mechanisms other than reptation, especially those which manifest themselves when the polymer undergoes flow. It is predicted that in the presence of strong flow extending to the nonlinear viscoelastic regime, the differences between star and linear polymers will be greatly reduced because of the influence of flow induced relaxation mechanisms such as convective constraint release (CCR) which is expected to dominate in both systems.

Wednesday 6:00 Humphrey Room PO36

Response of a poly(n-hexyl isocyanate)/p-xylene liquid crystalline system to an electric field and shear

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The effect of a high electric field on a solution of a lyotropic liquid crystalline polymer, poly(n-hexyl isocyanate) in xylene is presented. Application of a high voltage AC electric field (E) to the biphasic solution results in an elongation of the nematic domains in the field direction, the extent of eleongation varying with E^2. At a constant voltage, the extent of elongation, as measured by the aspect ratio, shows a decrease in the elongation varying inversely with the frequency in an exponential fashion. Upon the application of shear, the viscosity of the solution increases with increasing shear rate. In this study, we attempt to link this rheological behavior to the morphological changes in the nematic domain structure brought about by the presence of the electric field.

Wednesday 6:00 Humphrey Room PO37

Numerical simulation of the time-dependet flow of complex fluids in the cone and plate geometry

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The behavior of several complex fluids in a cone and plate geometry is investigated with a numerical simulation technique based on the deformation field method. The developed computer code is able to simulate the time-dependent flow for different models of viscoelastic fluids such as upper convective Maxwell, Doi-Edwards and Cates. The code was made using the FEM along with the Discrete Elastic-Viscous Split Stress formulation and the

penalty formulation. Numerical simulations of the Doi-Edwards and Cates models are shown for different sets of parameters.

Wednesday 6:00 Humphrey Room PO38

Electric field response of rigid poly(n-hexyl isocyanate) solutions

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The effects of concentration and molecular weight on the steady state electroviscosity and other rheological properties of solutions of poly(n-hexyl isocyanate) in p-xylene solutions have been examined experimentally and compared with scaling arguments from Doi's molecular theory of rigid rod polymers. PHIC samples with relatively low polydispersity were synthesized via the living polymerization technique of Patten and Novak in the range of 19 - 42 kDaltons. Because the chains are shorter than twice the persistence length, these polymers may be considered rigid rods. Electrorheological (ER) characterization at different values of dimensionless concentration c/c^* (c^* is the concentration where the isotropic phase becomes unstable) was performed in a Rheometrics ARES rheometer. Values of c/c^* ranged from the semidilute to the concentrated liquid crystalline regime. The viscosity ratio η_{on}/η_{off} ratio, where η_{on} is the viscosity achieved at maximum field and η_{off} is the zero field viscosity, is used to quantify the ER effect. All the PHIC solutions show a viscosity enhancement with the application of an electric field, which increases as concentration increases. For example, for a $c/c^* = 1.0$ there is a viscosity enhancement of 30.0, while for the $c/c^* =1.25$ it is 78.0. The relative increase in viscosity enhancement from $c/c^* =1.0$ to 1.25 was found to be within 10% of that predicted by the Doi theory.

Wednesday 6:00 Humphrey Room PO39

Sensitivity and stability of polymer extensional deformation processes using frequency response

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The sensitivity and stability of the final filament or film to the ongoing sinusoidal disturbances have been investigated in the viscoelastic fiber spinning and film casting processes, respectively, using frequency response method. First, alternative ways of solving the frequency response equation system were compared. Interestingly, in the cases examined, integrating the linearized equations over the length of the spinline to shoot at the take-up boundary conditions proved far more efficient than modal analysis using the eigenfunctions or solving the matrix problem from the entire length by either a direct method or an iterative one (GMRES). Amplification ratios or gains of the cross-sectional area of filament or film at the take-up position to any disturbances, representing the sensitivity of the flow system, show resonant peaks along the frequency regime, where the frequencies at these points directly correspond to the imaginary parts of the successive leading eigenvalues from the linear stability analysis. As shown in Jung et al., (1999) and Lee et al. (2001), the sensitivity results on the effect of various process conditions such as spinline cooling and fluid viscoelasticity, obtained by dynamic transient simulation have been corroborated in this study. Moreover, stability windows of the process systems adapted from the frequency response results have also been confirmed with those by the linear stability analysis.

Wednesday 6:00 Humphrey Room PO40

Hydrodynamic interaction between two cylinders in planar shear flow of viscoelastic fluid

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Particle-particle interaction is of great importance in the study of suspension rheology. In this research we have investigated the hydrodynamic interaction between two identical cylinders in viscoelastic fluid numerically as a model problem for the study of viscoelastic suspension. We consider two neutrally buoyant cylinders between two parallel plates filled with a Maxwell fluid and impose a shear flow. By solving the flow field, we determine the relative velocity of two cylinders. The result shows that cylinders move toward or away from the other depending upon the initial distance between them and that there is an equilibrium distance between two cylinders in viscoelastic fluid regardless of the initial distance. In the case of Newtonian fluid, there is no relative movement as expected. The results partly explain the chaining phenomena of spherical particles in shear flow of viscoelastic fluid.

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Wednesday 6:00 Humphrey Room PO41

Structural recovery and physical aging of glass-formers

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Volume recovery, enthalpy recovery, and the evolution of the creep compliance have been studied for three glass-forming materials, poly(ether imide), polystyrene, and selenium, at temperatures near and below the glass temperature. The times required to reach equilibrium for these different properties have been determined. The results indicate that although the three properties appear to reach equilibrium at the same time very near the glass temperature, the behavior appears to diverge several degrees below T_g. The generality and implications of the results will be discussed.

Wednesday 6:00 Humphrey Room PO42

Strain-induced change in dynamic mechanical spectrum of glassy poly(methyl methacrylate)

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Effect of large deformation on viscoelastic properties of glassy polymer was studied by means of dynamic mechanical analysis (DMA) on glassy poly(methyl methacrylate) (PMMA). Tensile specimens were prepared by thermal conditioning procedures with slow cooling and quenching through the glass transition temperature T_g, and then uniaxially stretched up to various amounts of strain. Stress-strain curves for slowly cooled specimens had a definite yield point, whereas those for quenched ones had no explicit yield point. By DMA, temperature dispersion of the storage modulus E' and the loss modulus E'' were obtained for stretched and also unstretched specimens. For slowly cooled specimens, temperature dispersion of E' almost unchanged by the imposition of strain, while E'' increased markedly with strain. The increase of E'' was observed at heating temperatures between β- and α-relaxation temperatures of the polymer. High values of E'' at temperatures between β- and α-temperatures are characteristic for a quenched polymer with non-equilibrium glassy structures. Hence, the increase in E'' of slowly cooled specimens due to tensile strains probably indicates that quasi-equilibrium glassy structures are gradually changed into non-equilibrium ones by the imposition of increasing strain. The increment of E'' of quenched specimens due to stretching was much smaller than that of slowly cooled specimens. This indicates that the strain induced much less structural change in quenched specimens. This is probably because the quenched specimens are non-equilibrium by nature. Yielding behavior was observed more definitely for slowly cooled specimens compared to that of quenched ones. Thus, it is concluded that yielding is a phenomenon ascribable to strain-induced structural change.

Wednesday 6:00 Humphrey Room PO44

Theory of viscoelastic free surface flow instability

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Flows of viscoelastic materials are highly susceptible to free surface instabilities. These show up as ribs in coating flows and fibrils in peeling and filament stretching flows. Based on the observation that these instabilities are always associated with a concave free surface, we present here a simple discussion of a generic mechanism responsible for them. The main result is that the combination of large tangential normal stress and curvature on a concave free surface result in a negative effective surface tension in the perturbation normal stress boundary condition. In more physical terms, an interface perturbation that locally thickens a film leads to a local accumulation of base state hoop

stress, which drives further thickening of the film. This result is independent of whether the elastic material is a liquid or solid. For viscoelastic liquids, a scaling analysis further shows that a wavelength selection mechanism for the instability exists independent of whether surface tension is present.

Wednesday 6:00 Humphrey Room PO45

Shear induced band texture and its effect on the viscoelasticity of a model thermotropic copolyester HBA/HQ/SA

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Observations of a model main chain thermotropic liquid crystalline polymer (TLCP3) using optical microscopy and rotational rheometry are presented along with the linking the evolution of melt textures with the flow behaviour. DSc and X-ray diffraction measurements show phase changes between 185 C and 162 C (nematic phase to a crystalline-nematic biphase) and between 162 C and ambient (crystalline-nematic biphase to semi-crystalline). There is also a high orientational ordering at 185 C and under shear at 170 C and 162 C due to the nematic content. A protocol involving low shear for t < 100 minutes and annealing for an equally long time produces almost perfect homotropic mono-domain textures, especially at 185 C when TLCP3 is nematic. Soft-solid behaviour is observed at 162 C and 170 C, with a crystalline to nematic phase transition under low and intermediate steady shears. The transition is reversible on crystallization, so long as the shear conditions remain within the linear viscoelastic region. Cooling from 180 C shows a crystallization-induced band texture with the crystallite bands mapping the director fields perpendicular to the original flow direction. Negative N_1 values are measured at 190 C and the N_1 and reduced stress behaviours linked with a band texture (bands parallel to the flow direction) observed at 190 C under oscillatory shear. The N_1 measurements cover the wagging and flow aligning regimes, but not the tumbling regime at very low shear rates. The band texture is initiated in regions of high Frank elastic energy in or near defects. A shear-induced phase transition at 230 C under oscillatory flow is also observed.

Wednesday 6:00 Humphrey Room PO46

Analysis of the interface between a viscoplastic and a Newtonian liquid flowing through a tube

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We study the displacement of one liquid, which initially fills a tube, by another. One of the liquids is Newtonian, while the other is viscoplastic. The liquids are considered imiscible. This kind of flow is found during cementing operations of petroleum wells, where different materials (such as drilling muds, cement pastes or washing fluids) flow in sequence through the column and through annular spaces. Drilling muds and cement pastes present viscoplastic behavior, while washing fluids are often Newtonian. To obtain a successful operation, the mixing between liquids, or, equivalently, the interface shape, should be as flat as possible. The interface configuration is strongly influenced by viscosity ratio and by rheological properties, such as yield stress and exponential index. Therefore, a study of the influence of these parameters in the interface configuration is an important and useful information for the petroleum industry. We present here the results of a preliminary study for the flow through a tube. We have performed flow visualization experiments, using a water-based Carbopol solution and oil as the working fluids. A VOF numerical investigation has also been performed, with the aid the FLUENT software. The effects of viscosity ratio, yield stress and Reynolds number on the interface configuration have been analyzed. Among other findings, it was observed that larger yield stress materials leads to more flat interfaces.

Wednesday 6:00 Humphrey Room PO47

Taylor-Couette instability of viscoplastic liquids

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The superposition of a circular Couette flow and a pressure-driven axial flow in an annulus occurs in many practical applications, such as catalytic chemical reactors, filtration devices, liquid-liquid extractors, journal bearings, and the return flow of drilling mud between the rotating drill string and the stationary wall in oil and gas well drilling. The curved streamlines of the circular Couette flow can cause a centrifugal instability leading to toroidal vortices, well known as Taylor vortices. The presence of these vortices changes the hydrodynamic and heat transfer characteristics of the process. Therefore, it is very important to be able to predict the onset of the instability. Most of the available theoretical and experimental analyses are for Newtonian and viscoelastic (polymeric solutions) liquids. In this work, the critical Taylor number in the case of no imposed axial flow at different geometrical configuration, i.e. inner-to-outer cylinder radius ratio, and different rheological parameters is determined by tracking the solution path as the Taylor number rises. The critical condition is characterized by the sudden appearance of an axial and radial velocity component. At each condition, the system of differential equation is solved by the Galerkin / finite element method. The resulting set of non-linear algebraic equations is solved by Newton's method.

Wednesday 6:00 Humphrey Room PO48

Deformation of multiple non-Newtonian drops in the axisymmetric 4:1 contraction flow

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The finite-element method is employed to analyze axisymmetric creeping motion of liquid drops moving along the centerline of the 4:1 contraction pipe. In the present study, deformation of multiple non-Newtonian drops suspended in non-Newtonian medium is taken into account, where a truncated power-law model is chosen as a viscosity function of non-Newtonian fluids. Using unstructured mesh generator combined with auto-remeshing techniques, we can describe the evolution of drop deformation in the flow field. Four different combinations of material parameters for both drop and medium are chosen in order to explain the dependence of drop deformation on material properties as well as the number of drops. In the case of a single drop deformation, the variation of speed of a drop according to material properties can be easily understood. When multiple drops are present in the medium, the deformation pattern and the speed of the foremost drop are varied due to the disturbance of following drops. In this regard, we extensively investigate and discuss the effect of non-Newtonian viscosity and the number of drops on the droplet deformation mechanism. The discussion on drop coalescence and break-up is not included due to the current limitation of auto-remeshing algorithm, and it is our ongoing research subject.

Wednesday 6:00 Humphrey Room PO49

Rheology and structure evolution during the flow of a medical-grade thermoplastic polyurethane

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The selection of operating conditions and geometry for the processing of thermoplastic polyurethane, TPU, is a complicated task. This complication arises from the relatively high melting temperature of the crystalline hard blocks and the oxidative crosslinking that occurs at temperatures that are relatively close to the melting temperature of the TPU. Here the rheology, extrusion, and structure development of a medical-grade TPU is documented. At temperatures 10-20°C lower than the melting temperature of the TPU the morphology of the hard blocks evolve to generate a reversible increase in elasticity and shear viscosity of the TPU with increasing residence time in this temperature range. At temperatures that are greater than the melting temperature the TPU undergoes a crosslinking reaction which gives rise to a permanent increase in the elasticity and the shear viscosity of the TPU. The

ramifications of the curing and morphology modification on rheology and the effects of the thermo-mechanical history experienced by the TPU during its processing on its structure development are elucidated.

Wednesday 6:00 Humphrey Room PO50

Rheology aspects of leather finishing formulations

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The rheological properties of leather finishing formulations and their effects on the physical properties of the finished leather have been investigated. The formulations and some of their ingredients were analyzed in the Ford Cup # 4, very common in Mexican tanneries, in the Brookfield viscosimeter, and in a rotational rheometer. The effects of the formulation parameters (solids content, resin-pigment ratio, resin hardness, and sort of pigment) on the viscosity behavior of the formulations followed similar trends. Statistically, the Ford viscosity was found non-significant. In contrast, the pigment color and the resin hardness as main effects were found significant when the samples were analyzed in the Brookfield viscosimeter and in the rotational rheometer. From the results in the rheometer, it was found that soft acrylic resins trigger shear thinning formulations, similar to the effect of the finishing pigments. In regard to the shear rates encountered in the process (~10,000 s^{-1}), this non-Newtonian behavior observed from the rheometer demonstrates that no reliable data can be obtained from the Ford Cup when assessing the flowing performance of leather finishing formulations. The viscosimeter Brookfield is a better option when a rheometer is not available since, taken separately, the consistency and power law indexes do not follow the same trends as the Brookfield viscosity. From the oscillatory tests in the rheometer, fluids containing soft resins and polymeric pigments produced formulations with elastic properties, especially at high solid contents. The soft resin governs the rheological behavior of the sample, especially when in presence of a polymeric black pigment. Regarding the leather finished samples, only tendencies could be obtained about the their physical properties and the rheology of the finishing formulations. The data scattering may be due to the natural non-uniformity associated with the tanned leather used in this investigation.

Wednesday 6:00 Humphrey Room PO51

Effect of borax concentration on the rheological properties of hyaluronic acid/poly(vinylahcohol) blend system

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Bioartifical polymeric materials represent a new class of polymeric material, based on blends of synthetic and biological polymers, designed with the purpose of producing new materials that have good mechanical properties and biocompatibility, and enhanced rheological properties with respect to the single components. Rheological properties of the blend which is composed of poly(vinyl alcohol)(PVA)-borax association(PVAs) as synthetic components and hyaluronic acid(HA) as biological components indicate the interaction between the two polymers. To control the degree of network structure formation of PVAs, various concentrations of borax are used from 0.1% to 1.0%. We investigate the effect of borax concentration in HA-PVAs blend through the rheological properties and microstructures. As borax concentration increases, the interactions are enhanced and it makes rheological properties increase. Microstructures of the blend are also affected. The transition from strain thinning to strain hardening appears at 0.5% as borax concentration increases. This behavior is confirmed by morphology of blends.

Wednesday 6:00 Humphrey Room PO52

Effects of surfactant and polymers on foam rheology – interfacial rheology aspects

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Foam is the leading consumer perceivable property for Personal Wash products. Tactile perception of the foam can be significantly altered by using different surfactants and polymers for foam generation. In this work, both air/liquid

interfacial rheology and bulk foam rheology have been studied for different surfactant/polymer systems. Interfacial shear viscosity and dilational elasticity were measured using CIR-100 surface viscometer and Film Rheometer respectively. Bulk foam rheology was measured using large-gap parallel plates for surfactant/polymer systems that generate rigid and mobile air/liquid interfaces. It was observed that the air/liquid interfacial rheology determines the perceived bulk foam rheology when other factors such as bubble size and gas fraction are kept constant. A phenomenological model is developed to correlate the interfacial and bulk rheology.

Wednesday 6:00 Humphrey Room PO53

Rheological behaviour and fatigue of alumina-based-chrome carbide composite coatings

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The paper addresses several topics concerning fatigue of composite coatings based on alumina-based ceramic coatings hardened by chrome carbide particles. Assuming power-law crack growth it is found that the crack growth rate decreases with the applied stress intensity factor in the initial stage of fatigue crack growth. Depending on the applied load and the amount of transformation, either the growth rate goes through a minimum before increasing to the normal crack regime, or the rate continues to decrease until the crack is arrested. Based on the parametric study a simple linear relationship between the applied load and the minimum transformation strength parameter necessary to cause crack arrest has been developed. It is be found useful in the design against fatigue by predicting the maximum toad at which crack arrest can be expected. Loading regimes has been supplied by indentation technique to be described under the principles of Hertzian theory. The above investigations have revealed a set of requirements that have to be used in proper development of rheological models of the composite. More importantly, rheological models using integral elastic-tenacious-plastic systems have been developed which provide plausible answers to the questions arising from fatigue observations and degradation of the coatings under indentation. The models also reveal an effect of cyclic and static loading in rheological and mechanical parameters of the composite, which may well be used in the safe design of hardened alumina ceramics against fatigue. The rheological models have been verified through comparison of calculations and experimental results obtained at indentation. Deformation rate, stress factors in both cases have been in good agreement one with another that supports the adequacy of the developed models.

Wednesday 6:00 Humphrey Room PO54

A comparison of the stress and birefringence growth of dilute, semi-dilute and concentrated polymer solutions in extensional flows

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A filament stretching rheometer is used to follow the evolution in the tensile force and the flow induced birefringence in polymeric fluid in a transient uniaxial elongational flow. Several monodisperse polystyrene solutions with concentrations between 0.025 wt.% to 12 wt.% are employed and the extensional rheology measurements are used to investigate the extent of hysteresis in the polymeric stress and anisotropy in molecular conformation during the imposed stretching and subsequent stress relaxation. For Deborah numbers above De > 0.5, a pronounced stress-conformation hysteresis is observed in the dilute polystyrene solution at large Hencky strains. Tests with a semi-dilute entangled polystyrene solution and a concentrated entangled polystyrene solution show that although the stress-optical rule is violated at large deformation rates and large strains, there is no evidence of any hysteresis during extension and subsequent relaxation. We interpret these observations in terms of the relative magnitude of the stretching rate as compared to the reptation time, and also as compared to the Rouse time scales for stretching of the entire chain or for a single entangled segment. These distinct time scales depend on the number of entanglements in the fluid and govern the different relaxation mechanisms that exist in entangled polymer solutions for the polymeric stress and the molecular conformation.

Wednesday 6:00 Humphrey Room PO55

A three-dimensional nonlinear viscoelastic constitutive model for UHMWPE used in medical implants

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Ultra high molecular weight polyethylene (UHMWPE) is used extensively in biomedical implant applications. The design of the UHMWPE components is critical to the longevity of the implant. Although the material has been used for decades as a biomedical material, its three-dimensional behavior is still not fully understood. At body temperature 37 C, UHMWPE is a nonlinear viscoelastic material-a composite of an amorphous rubbery phase reinforced by a more rigid crystalline phase. Here we examine the ability of the K-BKZ model to describe this complex material's viscoelastic response. Torsion measurements are performed to determine the time-dependent strain energy function from the torque and normal force responses using the Penn-Kearsley scaling approach. The time-dependent values of the strain energy function derivatives are then used in a Valanis-Landel formalism to form the K-BKZ kernal function and to predict the extensional response of the UHMWPE in constant rate of extension experiments. Comparison of predicted with measured response show that the K-BKZ model adequately describes the behavior of the UHMWPE even though it is a composite material.

Wednesday 6:00 Humphrey Room PO56

Influence of molecular architecture on extensional and shear rheology

Michael S. Owens, Christopher W. Macosko, and L. E. Scriven
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High molecular weight, polydisperse, branched polymer melts have been shown to cause extensional thickening (Munstedt & Laun), and solutions of high molecular weight polymers (Boger-liquids) also cause extensional thickening, but the influence of polydispersity and branching in these solutions is unknown. This behavior has implications in the atomization (misting) of coating liquids in forward roll coating film-splits operating at high speeds, i.e. 1000 m/min.

The goals of this work are to understand the relative contributions of branching, polydispersity, and molecular weight to shear and extensional rheology of low viscosity solutions, and how this influences misting in forward roll coating. To accomplish this a combination of polymer synthesis, molecular characterization, and rheological measurements are needed. Branched polydimethylsiloxane polymers have been synthesized using bi-functional vinyl PDMS and comb-like silicon-hydrogen/dimethyl copolymers. The extent of branching and molecular weight are examined by multi-angle light scattering, a controlled strain rheometer and an opposed nozzle indexer examine shear and extensional rheology, and misting is examined with high-speed cameras and a time-of-flight technique to measure particle size.

Rheologial behavior of Newtonian and non-Newtonian solution is compared to the tendency for these solution to mist in forward roll coating.

Wednesday 6:00 Humphrey Room PO57

Correlating strain hardening to extrusion foaming

Pieter Spitael and Christopher W. Macosko
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The importance of melt strength during the extrusion foaming of thermoplastic materials is addressed in this study. Rheological properties, and in particular strain hardening observed during extensional viscosity measurements, can have a significant impact in the foaming of thermoplastic materials. In the current work, the extensional viscosities of several polypropylene polymers and their blends were measured and compared to their relative foamability. Both a linear isotactic polypropylene and two branched polypropylenes with different extents of strain hardening were considered. Extensional viscosity was measured using an RME Elongational Rheometer (Rheometric Scientific). Foaming of the blends was subsequently carried out using a twin-screw extruder with carbon dioxide injected into the extruder barrel as the blowing agent.

It was found that a significant amount of extensional thickening, as quantified by a transient trouton ratio, prevailed even when the branched polypropylene was diluted with up to 75% linear polypropylene. Foams prepared from these blends were characterized in terms of bulk density, cell size and cell concentration. Lower density foams with larger cell concentrations were obtained by using blends of linear and branched polypropylene as compared to either the linear or branched homopolymer. Similarly, the extensional viscosity of a branched polystyrene was correlated to its foamability and compared to a linear polystyrene of similar molecular weight.

Wednesday 6:00 Humphrey Room PO58

New measurement technique for in-situ coating metrology

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The focus of current work is affixed on the development of a new measurement technique for the measurement of a coating thickness based on the phenomenon of the frustrated total internal reflection (F-TIR). Elimination of polymer surface instabilities (such as "sharkskin"), which develop during their processing (such as extrusion) are known to be effectively controlled by addition of polymer processing additives (PPA). The PPA facilitate elimination of the "sharkskin" by forming a coating layer at the die wall and thereby inducing a slip at the PPA/main-stream polymer interface. By utilizing the F-TIR approach we are able to sensitively capture the coating kinetics *in situ*. The estimated values for the thickness of a coating layer in steady state are significantly lower than numbers reported in the literature. Role of PPA content and its dispersion quality, as well as the effect of the temperature and the rate of shear will be discussed. Dependence of the coating kinetics on the viscosity ratio, the strength of polymer/PPA interaction on the molecular level will also be addressed.

Wednesday 6:00 Humphrey Room PO59

Improving falling-ball tests for viscosity determination

Shihai Feng, Alan L. Graham, James R. Abbott, and Patrick Reardon
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Experiments to determine the accuracy and reproducibility of the falling-ball test. A review of the relevant experimental work to date is presented as well as recommendations for improving both the accuracy and the reproducibility of the falling-ball test. New results exploring the wall and end effects and other possible anomalies in falling ball results due to non-Newtonian fluid rheology Present a formal error analysis of the falling-ball method. An analysis for error and reproducibility is presented. Recommendations based on current knowledge for improving.

Wednesday 6:00 Humphrey Room PO60

Practical comparison of differential viscoelastic constitutive equations in finite element modeling of planar 4:1 contraction flow

Jaewook Lee[1], Sungho Yoon[1], Youngdon Kwon[1], and Seejo Kim[2]
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Finite element modeling of viscoelastic planar 4:1 contraction flow (isothermal incompressible and creeping) with a sharp entrance corner is performed for the 8 most popular differential constitutive equations such as the Maxwell, Leonov, Giesekus, FENE-P, Larson, White-Metzner models and the Phan-Thien/Tanner(PTT) model of exponential and linear types. We have employed the discrete elastic viscous stress splitting (DEVSS) and streamline upwinding (SU) methods in order to split the extra stress tensor and also stabilize the convective term in the constitutive equation. For each constitutive model, we have computed the upper limit of the Deborah number under which numerical convergence is guaranteed. All the computational results are compared with those of mathematical analyses of constitutive equations from the viewpoint of stability. It is verified that mathematically well-posed constitutive equations proven from the stability analysis yield convergent numerical solutions in higher Deborah number flows. As a result, solutions for relatively high Deborah number flow can be obtained when one employs the Leonov, the PTT or the Giesekus constitutive equation as a viscoelastic field equation. By examining the region of solutions with loss of evolution (or viscoelastic change of type), the close relationship between numerical convergence and mathematical stability of model equations is also clearly demonstrated.

Wednesday 6:00 Humphrey Room PO61

VMB – a new approach to programming rheological testing

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Modern rheometers require sophisticated software in order to handle the increasingly complex requirements of researchers. The need for product formulation engineers to generate application relevant material parameters in the shortest test cycle requires custom testing methods that go beyond the typical "sweeps" offered by traditional testing firmware/software packages. These methods incorporate sophisticated program and flow logic, and take intelligent actions based on the analysis of data as it is measured.

In order to meet these needs Rheometric Scientific has developed a new approach to programming rheological tests and test methods, the VMB (Visual method builder). Instead of choosing from predefined sweep modes and test parameters, a completely programmable instrument has been developed with a rich instruction set of commands for actions such as motor and temperature control, and data acquisition. This allows the user to have a fine degree of control over all aspects of the test, and the flexibility to design new and more powerful test methods. In order to make such a system easy to use, test methods using these low level instructions are built using a graphical programming shell, which allows the methods to be built using simple drag-and-drop actions connecting these blocks together using a "plug and wire" metaphor. Programming the desired test methods then becomes nothing more than constructing a "flow-chart" to indicate the specific actions to take during operation.

The low-level rheometer instruction set is also combined with a powerful scripting system. The script allows for test flow decisions while sampling between 1 and 10kH and switching between transient and dynamic testing in less than 100ms. With this system we can export and import data to applications, and read incoming data streams from other devices such as A/D boards, temperature sensors, and access data analysis functions both within RSI Orchestrator software, or in third-party applications.

Wednesday 6:00 Humphrey Room PO62

Independent stress measurement extends the viscosity and frequency range of low viscosity fluids

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Measuring structure in low viscosity fluids like juices, dilute water-based systems, low viscosity inks, etc. can be very challenging. The reason for this is the inertia of the measuring device, which masks the elastic contributions of the weak structure in these materials.

Rheometers with an independent stress measurement (ISM) are not relying on the energy input of the actuator, which imposes the deformation onto the material to calculate the stress. Instead a separate transducer measures the reacting torque. The inertia of the actuator in this case does not effect the torque measurement.

The best parameter for evaluating to which extent the inertia of the actuator influences the time or frequency dependant response of a material in a rheometer without ISM is the ratio of torque used up by inertia to the total torque generated by the actuator. During transient experiments, the inertia is retarding the materials response and a Newtonian fluid shows a viscoelastic response with a characteristic time constant. In dynamic the inertia causes an additional phase shift, which effects the elastic modulus G'. For a typical rheometer with no ISM, this ratio of inertia torque to total torque typically is as high as 6 for a 10 cP fluid at 1 rad/s. For very light fluids, the rheometer often cannot do better than measure a steady or dynamic viscosity.

The inertia of a separate transducer is orders of magnitude lower than the inertia of the actuator due to its low mass. For the 2KFRT transducer from Rheometric Scientific Inc. the inertia correction is only 1.8% at 100 rad/s and is independent of the geometry, the strain and the material itself. Accurate measurements on water-like materials are possible up to 500 rad/s in dynamic or in a transient step rate experiments in less than 0.1 s. The material time/frequency dependence of these low viscosity fluids can be obtained as well as the elastic response, which is characteristic of the materials structure.

Wednesday 6:00 Humphrey Room PO63

Shear-free flows in a commercial rotational rheometer

Eric F. Brown
Paar Physica USA, Ashland, VA 23005

Extensional flows are found in many processing applications. However, it is difficult to design laboratory equipment that produces both reasonable extensional deformations and accurate data. Our company has developed a new control loop for the motor that controls the vertical movement of our measuring head. The head moves up and down with a well-defined speed. We have expanded this control to extensional measurements on viscoelastic materials. The capability of the instrument to perform uniaxial stretching and biaxial extension through lubricated squeezing will be examined.

Wednesday 6:00 Humphrey Room PO64

A normal stress sensor system for complete characterization of polymer shear flow properties

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There is a critical need for a commercial rheometer that can be used to measure all three shear flow properties of a molten thermoplastic. Currently available commercial rheometers can measure at best only two of the three independent shear flow properties, which are the viscosity, first normal stress difference (N1), and second normal stress difference (N2). The objective of the project is to demonstrate proof-of-principle for a novel rheometer plate with monolithically integrated miniature pressure sensors fabricated using microelectromechanical systems (MEMS) technology. It will be shown that this novel rheometer plate can be used to extend the capabilities of conventional rheometers, enabling measurement of all three shear flow properties with greater accuracy than previously possible. Furthermore, the innovative rheometer plate will allow smaller sample sizes to be used, with greater control over sample thickness during testing. Due to current instrument limitations, N1 and N2 are rarely measured, even though these propertes often have a strong influence on extrusion behavior and end-use properties of molten thermoplastics. Therefore, the proposed innovation should lead to better design and control of manufacturing processes with polymeric materials.

Wednesday 6:00 Humphrey Room PO65

Measurements of damping function for model polymer blends

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We present experimental results for the damping function of different model polymers (linears, stars, H's, and combs). We observe that different structures of well entangled polymers show similar damping. In entangled polymers the damping is well described by the Doi-Edwards theory; less entangled systems shows weaker damping, irrespective of polymer structure. In particular, an entangled melt of combs exhibits a damping function close to that for linear chains. Diluting the combs with linear chains leads to a more nearly constant damping function. Similar behavior has been observed for commercial LDPE.

Wednesday 6:00 Humphrey Room PO66

AFM-Based methodologies for interfacial nanorheology and nanotribology

Greg Haugstad[1], Craig Dykstra[2], Ronald H. Schmidt[2], Jon A. Hammerschmidt[2], Donna Staarup[2], Susheng Tan[2], Wayne L. Gladfelter[2], Christopher W. Macosko[3], and Philip Cole[3]
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We survey methodologies developed in our group for nanorheology/nanotribology of polymeric media invoking variants of atomic force microscopy. These techniques examine viscoelastic and viscoplastic response under

sinusoidal shear modulation, constant-velocity shear, normal tension/pull-off, or resonant intermittent contact. Independent variables include modulation amplitude/frequency, sliding velocity, load, temperature, humidity and molecular weight. Observables include shear response amplitude (fundamental and higher harmonics), sliding friction force, normal force, resonant normal amplitude/phase, and topographic modifications (plastic deformation). These techniques provide high spatial resolution and quantification of dissipative and relaxational behavior in the glassy, rubbery and melt regimes. Fourier analysis of shear-modulation response identifies and separates (a) linear from nonlinear (sliding, plastic) response, and (b) steady-state from creep response in the case of plastic deformation. A stick-to-sliding transition on polyvinyl alcohol (PVA) films is quantified, and found to depend on substrate proximity and water content. On polystyrene (PS) films our method is much more sensitive to plastic response than topographic image analysis. The role of entanglement is identified and exploited to profile a poly(methyl methacrylate)/poly(acrylonitrile) interface. Velocity dependent sliding friction on polydimethylsiloxane (PDMS) lubricant films is strongly dependent on film thickness. Along with tensile and pull-off measurements, a liquid-like to solid-like transition is identified at film thicknesses below 100 nm. Molecular weight dependence indicates a transition thickness of approximately 3Rg. The viscoelasticity of PDMS-based technologies, within two microns of a surface, are characterized using intermittent contact methods.

Wednesday 6:00 Humphrey Room PO67

Shear-induced mesostructure in nanoplatelet-polymer networks

S. Lin-Gibson[1], Gudrun Schmidt[2], H Kim[3], C C. Han[1], and Erik Hobbie[1]

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The mesoscale shear response of a model polymer-clay nanocomposite is measured using small-angle neutron scattering, light scattering, optical microscopy, and rheometry. As the shear disrupts the transient network that forms between clay and polymer, coupling between composition and shear stress leads to the formation of a spatially modulated domain pattern, while the clay platelets exhibit a shear-induced nematic phase with their surface normal parallel to the direction of vorticity. We suggest that the clay orients in response to a biaxial stress arising from viscous and elastic forces within macroscopic gel-like domains.

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Plenary Lectures

8:30 AM University Ballroom

Monday, October 14	**Do we really understand the coil stretch transition and extensional stresses of polymer solutions?** Eric S. Shaqfeh *Chemical & Mechanical Engineering, Stanford University*
Tuesday, October 15 *Bingham Lecture*	**Tubes and slip links: Two views of entangled polymer rheology** Ronald G. Larson *Chemical Engineering, University of Michigan*
Wednesday, October 16	**Rheophysics of wormlike micelles** Jean-François Berret *CNRS-Rhodia Complex Fluids Laboratory*

Social Program

Sunday, October 13	**Welcoming Reception** 7:00 PM – 9:00 PM University Ballroom (Radisson) *Sponsored by a generous contribution from TA Instruments*
Monday, October 14	**Society Reception** 7:00 PM – 9:00 PM Frederick R. Weisman Art Museum *Wine sponsored by a generous contribution from Thermo Haake*
Tuesday, October 15	**Business Meeting** 5:30 PM Ballroom A (Radisson)
	Awards Reception 7:00 PM – 8:00 PM McNamara Alumni Center *Wine sponsored by a generous contribution from Rheometric Scientific*
	Awards Banquet 8:00 PM McNamara Alumni Center
Wednesday, October 16	**Poster Session Refreshments** 6:00 PM – 8:00 PM Humphrey Room (Radisson) *Sponsored by a generous contribution from Paar Physica USA*