THE SOCIETY OF RHEOLOGY

70TH ANNUAL MEETING PROGRAM AND ABSTRACTS

Monterey Marriott
Monterey, California
October 4-8, 1998

Program Committee:

Patrick T. Mather (Co-Chair)
Air Force Research Lab
Ralph H. Colby (Co-Chair)
The Pennsylvania State University
Lynden Archer
Texas A&M University
Jon Bender
Lord Corporation
David V. Boger
D. V. Boger and Associates
Wesley R. Burghardt
Northwestern University
Robert J. Butera
DuPont Marshall Labs
Albert Co
University of Maine
A. Jeffrey Giacomin
University of Wisconsin
David James
University of Toronto
Rangaramanujam M. Kannan
Wayne State University
Bamin Khomami
Washington University
Stuart Kurtz
Union Carbide Corporation
Andre Lee
Michigan State University
Michael Mackay
The University of Queensland
Chuck Manke
Wayne State University
Gregory B. McKenna
NIST
Gareth McKinley
Massachusetts Institute of Technology
Bob Mendelson
Exxon Chemical Co.
Susan J. Muller
University of California
Michael Renardy
Virginia Tech
L. E. "Skip" Scriven
University of Minnesota
Eric S. G. Shaqfeh
Stanford University
Norman J. Wagner
University of Delaware
Lynn Walker
Carnegie-Mellon University
Shi-Qing Wang
Case Western Reserve University

Local Arrangements:

Gerald G. Fuller
Stanford University

Abstract Book Editor and Webmaster:

Albert Co, *University of Maine*

Meeting Schedule

Monday, October 5, 1998

8:30	G. Marrucci (PL1)			
9:20	Coffee			
9:45	NP1	GN1	EE1	SC1
10:10	NP2	GN2	EE2	SC2
10:35	NP3	GN3	EE3	SC3
11:00	NP4	GN4	EE4	SC4
11:25	NP5	GN5	EE5	SC5
11:50	Lunch			
1:30	NP6	GN6	EE6	SC6
1:55	NP7	GN7	EE7	SC7
2:20	NP8	GN8	EE8	SC8
2:45	NP9	GN9	EE9	SC9
3:10	Coffee			
3:35	NP10	GN10	EE10	IR1
4:00	NP11	GN11	EE11	IR2
4:25	NP12	GN12	EE12	IR3
4:50	NP13	GN13	EE13	IR4
5:15	End			
7:00	Society Reception			

Tuesday, October 6, 1998

8:30	J. M. Dealy (PL2)			
9:20	Coffee			
9:45	VP1	GN14	EE14	IR5
10:10	VP2	GN15	EE15	IR6
10:35	VP3	GN16	EE16	IR7
11:00	VP4	GN17	EE17	IR8
11:25	VP5	GN18	EE18	IR9
11:50	Lunch			
1:30	VP6	CF1	EE19	EX1
1:55	VP7	CF2	EE20	EX2
2:20	VP8	CF3	EE21	EX3
2:45	VP9	CF4	EE22	EX4
3:10	Coffee			
3:35	VP10	CF5	SL1	EX5
4:00	VP11	CF6	SL2	EX6
4:25	VP12	CF7	SL3	EX7
4:50	VP13	CF8	SL4	EX8
5:15	End			
5:30	Business Meeting			
7:00	Awards Reception			
8:00	Awards Banquet			

Wednesday, October 7, 1998

8:30	S. Granick (PL3)			
9:20	Coffee			
9:45	SE1	CF9	SL5	AN1
10:10	SE2	CF10	SL6	AN2
10:35	SE3	CF11	SL7	AN3
11:00	SE4	CF12	SL8	AN4
11:25	SE5	CF13	SL9	AN5
11:50	Lunch			
1:30	SE6	CF14	SL10	AN6
1:55	SE7	CF15	SL11	AN7
2:20	SE8	CF16	SL12	AN8
2:45	SE9	CF17	SL13	AN9
3:10	Coffee			
3:35	SE10	CF18	EM1	AN10
4:00	SE11	CF19	EM2	AN11
4:25	SE12	CF20	EM3	AN12
4:50	SE13	CF21	EM4	AN13
5:15	End			
5:30	Poster Session & Refreshments			

Thursday, October 8, 1998

8:05	SE14	FS1	EM5	AN14
8:30	SE15	FS2	EM6	AN15
8:55	SE16	FS3	EM7	AN16
9:20	SE17	FS4	EM8	AN17
9:45	Coffee			
10:10	SE18	FS5	JA1	AN18
10:35	SE19	FS6	JA2	AN19
11:00	SE20	FS7	JA3	AN20
11:25	SE21	FS8	JA4	AN21
11:50	SE22	FS9	JA5	AN22
12:15	End			

Session Codes

AN = Analytical and Numerical Solutions to Flow Problems
CF = Coupling Flow and Order in Fluids
EE = Extensional and Elongational Flow
EM = Rheology and Microstructure of Electro and Magneto-Rheological Fluids
EX = New Experimental Methods
FS = Polymer Friction, Slippage, and Dynamics Near Surfaces
GN = General Session
IR = Interfacial Rheology and Rheological Modifiers
JA = Jet Breakup, Atomization, and Spraying of Non-Newtonian Liquids
NP = Polymers with Novel Architectures
PL = Plenary Lectures
SC = Solutions and Coating Rheology
SE = Suspensions and Emulsions
SL = Rheology of Solids
VP = Viscoelastic Processing Flows: Theory and Experiment

Contents

This publication was generated with scripts developed by Albert Co. The contents of this publication were extracted from the database of The Society of Rheology abstract submission web site at http://www.umecheme.maine.edu/sorabst/.

Monday Morning

Symposium PL
Plenary Lectures

Monday 8:30 Steinbeck Forum PL1

RECENT PROGRESS IN THE THEORY OF ENTANGLED POLYMERS IN FAST FLOWS

Giuseppe Marrucci
Chemical Engineering, University of Naples, Napoli 80125, Italy

The tremendous success of the theory of Doi and Edwards for entangled polymers has long been marred by the prediction of an excessive shear thinning. In recent years, however, we examined an additional relaxation mechanism that becomes important in fast flows, where it strongly reduces shear thinning. Ianniruberto and myself named the mechanism "convective constraint release" or CCR. It consists in the fact that the relative motion between neighboring chains due to the velocity gradient removes entanglements at a rate that soon becomes competitive with reptation. This additional relaxation mechanism reduces chain orientation as induced by shear, thus diminishing the shear-thinning effect. The resulting tendency is for the shear stress to level off, rather than decrease with increasing shear rate as in the original Doi-Edwards model. Very recently, Larson, Mead and Doi have formulated a constitutive equation based on CCR, which also includes the effect of chain stretching at even higher shear rates. They have also highlighted the effect of tube length fluctuations on the shape of the flow curve at lower shear rates. Here, after summarizing the above progress, we discuss further aspects of the tube model that perhaps require improvement. We are motivated by residual discrepancies that are observed between data and model predictions.

Symposium NP
Polymers with Novel Architectures

Organizers: Patrick T. Mather and Michael Mackay

Monday 9:45 San Carlos I NP1

CHARACTERIZATION OF DENDRIMERS AS MODEL POLYMERS WITH UNIQUE PROPERTIES

Eric J. Amis, Barry J. Bauer, Ty J. Prosa, and Andreas Topp
Polymer Division, National Institute of Standards and Technology, Gaithersburg, MD

Dendrimers represent a new class of polymers having shape and structural uniformity. Unlike typical polymers that we model as strings of flexibly linked beads, the pattern of regular branching in dendrimers creates molecules with special properties. X-ray and neutron scattering methods have been used to characterize dendrimers in solution, in bulk, in mixtures with linear polymers, and incorporated into networks. As a result of their unique structure, these molecules have interior and exterior segments that can be designed with different chemical functionality. The consequence of this dendritic copolymer structure has implications for both properties and potential applications. Because they can be engineered reliably they can also be powerful research tools.

Monday 10:10 San Carlos I NP2

STRUCTURE AND DYNAMICS OF MULTIARM STAR POLYMERS

Dimitris Vlassopoulos[1], G. Fytas[1], T. Pakula[2], A.N. Semenov[3], and J. Roovers[4]

[1]Institute of Electronic Structure and Laser, FO.R.T.H., Crete, Greece; [2]Max-Planck Institut für Polymerforschung, Mainz, Germany; [3]Dept. Applied Mathematics, University of Leeds, Leeds, United Kingdom; [4]Institute for Environmental Chemistry, National Research Council, Ottawa, Ontario, Canada

We probe the structure of model star polymer melts of varying arm functionality (f) and molecular weight (Ma) with SAXS. Due to topological constraints, the monomer density distribution is inhomogeneous and liquid-like ordering is detected. The signature of ordering is reflected in the linear viscoelastic spectra as a second terminal relaxation process at very low frequencies, in addition to the faster arm relaxation. The dependence of both modes on f and Ma, as well as their interplay, are established. With the aid of Monte Carlo computer simulations and a mean field scaling theory we associate the slow structural mode with the cooperative rearrangements of the ordered stars, and thus explain its strong molecular weight dependence. Based on these results, we propose a general picture for the relaxation of complex mesoscopic systems such as stars, block copolymer micelles, microgels and crew-cut aggregates. This suggests that by tailoring the functionality and arm size of this new class of model soft spheres at the chemistry level, a promising route to bridge the gap between polymer and colloids science could open.

Monday 10:35 San Carlos I NP3

THE INFLUENCE OF DENDRIMERS AND HYPERBRANCHED POLYMERS ON THE THERMODYNAMICS AND RHEOLOGY OF LINEAR POLYMERS

Igor Bodnar[1], Young H. Kim[2], and Norman J. Wagner[1]

[1]Dept. of Chemical Engineering, University of Delaware, Newark, DE 19716; [2]Experimental Station, DuPont Central Research & Development, Wilmington, DE 19880

Hyperbranched polymers (HBPs) are a new class of polymers of which the properties are thought to lay somewhere between linear polymers and dendrimers. There have been much progresses in the structural understanding and the methods of synthesis of these polymers. However, functional understanding and utility of these polymers are still in infancy. Better understanding of the physical properties of HBPs and dendrimers is therefore essential for the further development of these materials.

We studied the solubility and miscibility of dendrimers and HBPs in solution and blends with linear polymers. Commercially available DB(PA)32 en DB(PA)64 (4th and 5th generation DSM-dendrimers) were derivatized with acetyl-chloride and deuterated acetyl-chloride. These were studied with neutron scattering at different concentrations and in aqueous solutions of the linear polymer poly(ethyleneoxide) (Mw=300k). The solution rheology was also measured. The results are interpreted in terms of polymer as well as colloid models. The microstructure of the mixtures, as determined with Small Angle Neutron Scattering (SANS), is to be correlated to the rheological behavior. Comparisons with model experiments involving linear, dendritic, and colloidal analogs helps to define the efficacy of hyperbranched polymers as rheology modifiers.

Keywords: Dendrimers, Hyperbranched Polymers, Rheology, SANS, Polymer Blends.

Monday 11:00 San Carlos I NP4

THE EFFECT OF LONG CHAIN BRANCHING ON THE RHEOLOGICAL BEHAVIOR OF METALLOCENE POLYETHYLENES

Paula M. Wood-Adams and John M. Dealy

Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada

Constrained Geometry metallocene catalysts make it possible to control independently molecular weight (MW), molecular weight distribution (MWD), homogeneity of short chain branching, and degree of long chain branching (LCB). This catalyst technology therefore provides us with a unique opportunity to study the effects of molecular structure on the rheological behavior of polyethylene. In particular the effects of low levels of long chain branching (LCB) have never been studied in commercial polyethylenes, because it was impossible to vary the degree of

branching while maintaining the backbone molecular weight and molecular weight distribution using traditional polymerization techniques.

Nine metallocene polyethylenes with approximately the same MWDs but varying degrees of LCB were subjected to an intensive study including linear viscoelastic behavior and nonlinear shear and extensional flow behavior. Using these results, it was found that low levels of LCB manifest themselves mostly in the linear regime and not in nonlinear extensional flow behavior as was previously thought. It was also found that these branched materials followed the Cox-Merz rule and the Gleissle mirror relations. Separable stress relaxation behavior was exhibited in step strain experiments. LCB increased the nonlinearity in the fluids' response to large amplitude oscillatory shear.

A procedure was developed for quantifying LCB using linear viscoelastic data and backbone MWD information. Such a procedure is particularly important in the case of ethylene-octene copolymers for which it is difficult to measure the degree of long chain branching using nuclear magnetic resonance techniques.

Monday 11:25 San Carlos I NP5

PREDICTING THE LINEAR VISCOELASTIC BEHAVIOR OF STAR POLYMERS UTILIZING AN EXTENSION OF THE DOUBLE REPTATION THEORY WITH NO ADJUSTABLE PARAMETERS

Timothy J. Van Dyke[1], David W. Mead[2], and Ronald G. Larson[3]
[1]Applied Mechanics and Engineering Science, University of California - San Diego, San Diego, CA 92093-0411; [2]Mechanical Engineering, University of Michigan at Ann Arbor, Ann Arbor, MI 48109-2125; [3]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136

Monodisperse star polymers provide a discriminating test of molecular theories for polymer relaxation in that for stars reptation is suppressed and relaxation occurs via contour length fluctuation along with constraint release. Hence, only if these fluctuations are properly described will a model for star polymers be successful. A correct model for contour length fluctuations can then be incorporated with confidence into molecular models with arbitrary architectures.

We present a new binary contact method for predicting the linear viscoelastic properties of star polymers which includes contour length fluctuations and the concept of dynamic dilution in a straight forward manner. This method can readily be extended to polydispersity and included in models for linear polymers. It also has the great advantage that it can be extended systematically to the nonlinear regime. Predictions of this model for the linear viscoelastic properties of monodisperse flexible star polymers are compared to experimental results for different polymer systems and the fit is seen to be quite remarkable, especially when it is considered that there are no adjustable parameters in the model (*i.e.*, literature values for different material constants were used without adjustment in making the predictions).

Symposium GN
General Session

Organizer: Wesley R. Burghardt

Monday 9:45 San Carlos III GN1

EXAMINATION OF A NEW MOLECULAR MODEL FOR POLYDISPERSE SYSTEMS OF LINEAR FLEXIBLE POLYMER IN STEADY AND TRANSIENT SHEAR FLOWS

James J. Driscoll[1], David W. Mead[1], Ronald G. Larson[2], Masao Doi[3], and Ali Berker[4]
[1]Mechanical Engineering, University of Michigan at Ann Arbor, Ann Arbor, MI 48109-2125; [2]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136; [3]Computational Physics, University of Nagoya, Nagoya 464, Japan; [4]Adhesive Technologies Center, 3M Co., St. Paul, MN 55144-1000

A new molecular model has been developed for polydisperse systems of flexible polymer based on a generalization of the binary contact model originally presented by Tsenoglou. Tsenoglous model accounts for reptation induced constraint release in small deformations only and ignores all other constraint release mechanisms. Our model generalizes Tsenoglous model to account for two constraint release mechanisms, reptation and chain retraction and hence is applicable to non-linear deformations. We explore the predictions of this model with respect to well established steady state and transient non-linear empirical rheological relations, specifically, the Cox-Merz rule relating the steady flow curve to the dynamic moduli and the Gliessle mirror relations for transient effects.

Monday 10:10 San Carlos III GN2

STRESS PLATEAU BEHAVIOR IN FAST FLOW OF MONODISPERSE POLYMERIC FLUIDS

Xiaoping Yang and Shi-Qing Wang
Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Both steady and oscillatory shear measurements have been carried out to study the constitutive stress plateau behavior of monodisperse polymer melts and concentrated solutions. The nature of the "stress plateau" has been under active investigation over the past decade by several theoretical groups in the community [1-3]. Experimental reports of "stress plateau" in polymer melts and solutions are scarce to find in the literature. We have selected a few model systems to experimentally explore the origin of the fast flow behavior using both parallel-plate and capillary rheometry. In particular, we probe the question of whether chain disentanglement occurs discontinuously in the bulk to produce the observed plateau and when the Cox-Merz rule breaks down.

[1] M. Cates, T. C. B. McLeish and G. Marrucci, Europhys. Lett. 21, 451 (1993).
[2] G. Marrucci, J. Non-Newtonian Fluid Mech. 62, 279; 65, 241 (1996b).
[3] R. Larson, D. Mead and M. Doi, unpublished.

Monday 10:35 San Carlos III GN3

RHEOLOGY OF PERFLUOROPOLYETHER/POLY 1H,1H-PENTADECAFLUOROOCTYL METHACRYLATE BLENDS

Tom E. Karis
K13/E1, IBM ARC, San Jose, CA 95120

Fluoropolymer films are widely used as a low surface energy barrier to prevent fluid migration along solid surfaces. The fluid is typically a lubricant, and the fluoropolymer film is solution cast onto metal surfaces surrounding a bushing or bearing containing the lubricant. This study considers blends of perfluoropolyether (PFPE) oil and a 1H,1H-pentadecafluorooctyl methacrylate polymer (PFOM). The PFOM should not flow at elevated temperatures for long periods of time in the presence of the PFPE. The PFPE plasticizes the PFOM. Flow may be induced by gravity, centrifugal, or inertial forces. The steady shear creep compliance and oscillatory shear moduli of PFPE/PFOM blends were measured between 20 and 90 C. The viscoelastic properties at each temperature were superimposed to obtain a temperature master curve at each concentration. Superposition was also found to be possible by shifting the temperature master curves at each concentration to obtain a concentration-temperature master curve. The results are discussed in terms of thermodynamics and the temperature- concentration shift factors.

Monday 11:00 San Carlos III GN4

EFFECTS OF WAX CRYSTALLIZATION ON THE FLOW OF MINERAL OILS

Richard M. Webber

Research & Development, Lubrizol Corporation, Wickliffe, OH 44092

The formation of wax crystals in mineral oils at low temperatures due to poor solubility of paraffinic components leads to oil rheology that is strongly dependent on stress and temperature history. For example, under quiescent cooling wax crystallization can lead to the development of a yield stress. How temperature history and oil composition affect wax crystallization and therefore rheology are important issues in the lubricant industry where lubricating oils must be formulated to meet particular low temperature rheological standards. In mineral oils containing no performance chemical additives, viscosity as a function of decreasing temperature shows a high activation energy transition region. The onset temperature (T_c) to the high activation energy viscosity-temperature region corresponds to the temperature at which wax crystals become microscopically visible. Both T_c and the activation energy in the transition region depend on the cooling rate, decreasing and increasing respectively with increasing cooling rate. The high activation energy transition persists for a few degrees and is then followed by a broad temperature range where the viscosity-temperature activation energy is substantially weaker than that in the transition, but greater than that observed at $T > T_c$. We use a simple model for homogeneous nucleation to discuss how wax crystallization in an oil with a molecular weight distribution of wax forming paraffins is reflected in the low temperature rheology of the oil.

Monday 11:25 San Carlos III GN5

BLENDS OF LINEAR AND BRANCHED POLYETHYLENES

Heon Sang Lee and Morton M. Denn

Materials Sciences Division/Department of Chemical Engineering, Lawrence Berkeley National Lab. & University of California at Berkeley, Berkeley, CA 94720-1462

We have studied the linear-viscoelastic and thermal properties of binary and ternary blends of high-density (HDPE), linear low-density (LLDPE), and low-density (LDPE) polyethylenes in the melt and solid state. HDPE-LLDPE blends exhibit a single melting peak and a single, sharp gamma transition, and the dynamic melt rheology is well-characterized by the single-phase double-reptation model. We therefore conclude that HDPE- LLDPE blends are homogeneous in the melt and in both crystalline and amorphous regions in the solid state. LLDPE- LDPE blends exhibit two melting peaks at all compositions, while the blends show a single gamma-relaxation peak for LLDPE-rich blends and two peaks for LDPE-rich compositions. The melt viscoelasticity is well-characterized by the Palierne two-phase emulsion model. These results suggest that LLDPE- LDPE blends are immiscible in the melt and in the crystalline region in the solid, with partial miscibility in the amorphous region in the solid. HDPE-LDPE blends exhibit single melting and gamma-relaxation peaks for HDPE-rich compositions, while two melting and gamma-relaxation peaks occur for LDPE-rich compositions, indicating that HDPE-LDPE blends are partially miscible in both the amorphous and crystalline regions in the solid. The storage and loss moduli in the melt both decrease exponentially with increasing HDPE fraction at low and high frequencies. Finally, ternary blends containing a critical concentration of HDPE show a single melting peak, indicating that HDPE serves as a compatabilizing agent for immiscible LLDPE-LDPE blends.

Symposium EE
Extensional and Elongational Flow

Organizers: David James and Gareth McKinley

Monday 9:45 San Carlos II EE1

ISSUES IN EXTENSIONAL RHEOMETRY

Tam Sridhar
Chemical Engineering, Monash University, Clayton, Victoria 3168, Australia

The last decade has witnessed an explosion of activity in the area of extensional rheology of polymer solutions. Equally pleasing is the concurrent advances being made both in theoretical modelling of such flows using stochastic simulations and Brownian configurational fields and also in the experimental realisation of such flows. The filament stretching rheometer introduced by Sridhar et al (1991) and Tirtaatmadja and Sridhar (1993) has proved to be a versatile tool for experimental studies. Examination of this technique experimentally (Spiegelberg et al., 1966; Soloman and Muller, 1996 and Van Nieuwkoop and Von Czernicki, 1996) and by simulation of the flow field (Sizaire and Legat, 1997, Kolte et al., 1997, Yao and McKinley, 1998) has contributed to an understanding of the limitations of this technique. This presentation will attempt to review this area and illustrate the significant new body of knowledge arising from these and other studies. Several intriguing results which expose the limitations of currently used constitutive models will be presented. Recent results on birefringence and stress for a round robin fluid created by Professor Muller will also be presented.

References:

M.I. Kolte, H.K. Ramussen & O. Hassager, Rheol. Acta 36, 285 (1997).
J. Van Nieuwkoop & M. Von Czernicki, JNNFM, 67, 105 (1996).
M.J. Solomon & S.J. Muller, J. Rheol., 40, 837 (1996).
R. Sizaire & V. Legat, JNNFM, 71, 89 (1997).
S.H. Spiegelberg, D.C. Ables & G.H. McKinley, JNNFM, 64, 229 (1996).
T. Sridhar, V. Tirtaatmadja, D.A. Nguyen & R.K. Gupta, JNNFM, 20, 271 (1991).
V. Tirtaatmadja & T. Sridhar, J. Rheol., 37, 1081 (1993).
M. Yao & G.H. McKinley, JNNFM, 74, 47 (1998).

Monday 10:10 San Carlos II EE2

THE TRANSIENT EXTENSIONAL VISCOSITY OF DILUTE AND SEMI-DILUTE POLYMER SOLUTIONS MEASURED WITH A FILAMENT STRETCHING RHEOMETER

Kurt W. Koelling and David S. Shackleford
Dept. of Chemical Engineering, The Ohio State University, Columbus, OH 43210

A filament stretching extensional rheometer is used to measure the transient extensional viscosity of a series of polybutene based Boger fluids. The test fluids include 12 dilute and semi-dilute solutions of 4.2×10^5, 1.2×10^6 or 4.7×10^6 g/mol polyisobutylene dissolved in a common solvent consisiting of 95.2% polybutene and 4.8% tetradecane. The critical overlap concentration was determined experimentally using intrinsic viscosity measurements for this system of polymer solutions, and test fluids were prepared which vary in concentration above and below this value. These fluids were then tested with a filament stretching device designed to reach Hencky strains as high as 7 at stretching rates ranging from 0.5 to 6 s^{-1}, in order to reach steady state values of extensional viscosity. Steady-state Trouton ratio increases from 2×10^3 to 1×10^4 as the 4.7×10^6 g/mol polyisobutylene concentration increases from 0.012 to 0.59 wt%. Steady-state Trouton ratio is also found to increase from 10^2 to 10^4 as polyisobutylene molecular weight increases from 4.2×10^5 to 4.7×10^6 g/mol. These experimental results are compared to Batchelor's model for a suspension of rigid rods. The influence of inter- and intramolecular entanglements on steady-state extensional viscosity are discussed.

Monday 10:35 San Carlos II EE3

NECKING AND BREAKUP OF VISCOELASTIC FLUID FILAMENTS IN FILAMENT STRETCHING DEVICES DURING STRETCHING AND SUBSEQUENT STRESS RELAXATION

Shelley L. Anna[1], Minwu Yao[2], and Gareth H. McKinley[1]

[1]Dept. of Mechanical Engineering, M.I.T., Cambridge, MA 02139; [2]Computational Materials Lab., Ohio Aerospace Institute, Brookpark, OH 44142

We investigate the transient uniaxial stress growth of polymer melts and concentrated solutions in a filament stretching device. Such fluids exhibit much less significant strain-hardening than is typically observed in dilute and semi-dilute solutions such as Boger fluids, and the need for comparison between experimental observation and numerical calculation of the resulting fluid dynamics is correspondingly greater. There are three distinct dynamical regions that can be distinguished during a prototypical stretching and relaxation experiment: (i) during the stretching phase, the filament undergoes a spatially nonhomogeneous extensional deformation, the tensile stress difference increases and the sample develops a 'necked configuration' with a profile that depends on the degree of strain-hardening in the fluid; (ii) following the cessation of stretching, there is a short period during which there is little fluid motion and the tensile stresses in the column rapidly relax as predicted following cessation of homogenous uniaxial elongation; (iii) finally, at longer times, fluid motion in the filament leads to further necking and the column can undergo rupture into two distinct domains attached to either endplate. The onset of pronounced filament necking during the imposed elongation and the time to breakup following cessation of stretching are both found to be sensitive functions of the transient extensional viscosity and the magnitude of strain-hardening in the test fluid. Finite element calculations provide good agreement with the experiments and also with a one-dimensional slender filament theory for break-up of a viscoelastic fluid column. Finally, we show how this one-dimensional theory can also be used to derive an experimental motion control algorithm for systematically achieving a homogeneous uniaxial deformation in any viscoelastic fluid undergoing stretching in a filament stretching device.

Monday 11:00 San Carlos II EE4

FLOW LIGHT SCATTERING STUDIES OF POLYMER COIL CONFORMATION IN SOLUTIONS IN EXTENSIONAL FLOW

Ellen C. Lee and Susan J. Muller

Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720

The dynamics of isolated polymer chains in dilute solution under steady, planar extensional flow were investigated by means of flow light scattering. Both the orientation and deformation of the chains during steady flow were determined by analyzing the angular dependence of the scattered light intensity. The extensional flow field was imparted on the polymeric fluids by a stagnation point flow in the center of a four-roll mill apparatus. The fluids studied were nearly monodisperse high molecular weight polystyrenes of various molecular weights dissolved in either the viscous solvent dioctyl phthalate, or a mixed solvent of low molecular weight polystyrene and dioctyl phthalate. The flow field in a Newtonian fluid of seeded glycerin was also examined by both flow dynamic light scattering (Fuller et al., *Journal of Fluid Mechanics*, **100**, 555 (1980)) and flow visualization techniques to confirm the extensional flow field. Flow dynamic light scattering and flow visualization results verified that the field generated by the four-roll mill was a reasonable approximation of planar extensional flow under the conditions investigated. Flow (static) light scattering results confirmed that the polymer chains aligned completely with the stretch direction, as expected for this type of flow. The deformation of the chains, however, was significantly less than predicted by kinetic theory models. Also studied were the effects of the molecular weight and solvent quality on the deformation of the polymer chains. Comparisons are drawn between the strong extensional flow field studied here and a steady shearing flow examined previously (Lee et al., *Macromolecules*, **30**, 7313 (1997)).

Monday 11:25 San Carlos II EE5

OPTICAL ANISOTROPY OF MOBILE VISCOELASTIC LIQUIDS ON TRANSIENT PLANAR EXTENSION FLOW

Tsutomu Takahashi[1], Hideki Ohkouchi[2], Manabu Adachi[1], and Masataka Shirakashi[1]
[1]Department of Mechanical Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan; [2]Osaka Engineering Research Laboratory, Teijin Limited, Ibaraki, Osaka 567-0006, Japan

The transient extensional behavior of mobile viscoelastic liquids, which have less than 10 Pa-s in viscosity, was investigated. A new rheo-optical analyzer combined with a squeeze flow cell and an optical analyzer was designed for this purpose. Although the four-wheel mill flow cell and the convergent flow cell are good instruments for measurements of the steady extensional properties of such mobile liquids, they are hard to investigate the transient extensional behavior because of the inertia effect. The new instrument can produce the transient planar extension flow by the squeezing two parallel plates. A computer controls the squeezing rate to keep a constant extension rate during experiment. A laser beam from the optical analyzer transmits through the stagnation line between the plates and probes the optical properties, the orientation angle and the birefringence of the squeezed sample. Two surfactant solutions, CPyCl/NaSal and CTAB/NaSal, are used as samples. Both surfactants form the worm-like micelles and show strong viscoelasticity. The orientation angle kept zero during the squeezing the plates in vertical direction. It demonstrates that the laser beam transmitted through the stagnation point correctly and the sample located on the beam path was stretched horizontal direction during the experiment. The result of the birefringence kept a constant value except the start-up and relaxation regions. On the start-up region of the test for CTAB/NaSal, the birefringence showed the over-shot at the high extension rate as similar as behavior at simple shear. The extension stress was calculated from the birefringence if the stress-optic rule was applicable at the rate and the extensional viscosity was also estimated.

Symposium SC
Solutions and Coating Rheology

Organizers: Eric S. G. Shaqfeh and L. E. "Skip" Scriven

Monday 9:45 Los Angeles SC1

RHEO-MECHANICAL AND RHEO-OPTICAL CHARACTERIZATION OF VISCOELASTIC POLYMER SOLUTIONS

W.-Michael Kulicke and Oliver Arendt
Institute of Technical and Macromolecular Chemistry, University of Hamburg, Hamburg 20146, Germany

The molecular mechanism for the dependence on shear rate of polymer solutions has been subject to numerous investigations. If one considers diluted solutions, a decrease of the excluded volume and an increase of the intramolecular interactions are made responsible for the non-Newtonian behavior.

As structural viscosity was also observed in theta-solvents, where the excluded volume is zero, hydrodynamic interactions were considered. Furthermore, there were ideas about the finite expandability of the macromolecules in the direction of shear, esp. the dumbbell model of Bird and coworkers. But an application of this relatively simple model for semi-diluted polymer solutions is impossible, as the polymer concentration is not taken into consideration in the theoretical part.

Therefore, we would like to show that rheo-*optical* investigations that analyse the flow birefringence and flow dichroism can be used to draw conclusions about the mobility and orientation of the polymer as a function of the shear rate. It is possible to characterize the dynamic behaviour of local structures (polymer segments and polymer aggregates), determine intermolecular and intramolecular interactions, and detect changes in the solution structure.

This is going to be demonstrated at polystyrene in toluene and at mixtures of biopolymers and hydrocolloids (e.g. waxy maize starch and κ-carrageenan, carboxymethylcellulose or locust bean gum and κ-carrageenan).

Monday 10:10 Los Angeles SC2

NONLINEAR VISCOELASTICITY OF POLYMER SOLUTIONS: TORQUE AND NORMAL FORCE MEASUREMENTS IN POLYSTYRENE/ORTHO-TERPHENYL MIXTURES

Vannarong Soulivong and Gregory B. McKenna
Polymers Division, NIST, Gaithersburg, MD 20899

The nonlinear rheology of polymers has been extensively studied as a function of molecular architecture and temperature. In particular, shear rate dependence of the viscosity and first normal stress difference have been extensively examined as have the so-called damping function in time-strain separable Wagner or Doi-Edwards types of single integral constitutive model. At the same time, relatively few systematic evaluations of polymer concentration on the same material parameters have been performed. Here we examine the impact of polymer concentration on the viscoelastic response of the polystyrene/ortho-terphenyl system. We probe the response primarily using torsional measurements and simultaneously recording the torque and the normal force. Following the application of the Penn and Kearsley Scaling Law for elastic cylinders to viscoelasticty media used by McKenna and Zapas, we obtain the time dependent strain potential function derivatives. This approach can also be formally arrived at from the K-BKZ single integral model. Results will be reported for concentrations of 25, 50 and 75 % polystyrene at 35 C. Analysis of the data within the frameworks of both damping function and the time- dependent strain potential function approaches will be discussed.

Monday 10:35 Los Angeles SC3

THE DYNAMICS OF ENTANGLED POLYMER SOLUTIONS SUBJECT TO ABRUPT CHANGES OF SHEAR RATE

James P. Oberhauser and Gary Leal
Chemical Engineering, University of California - Santa Barbara, Santa Barbara, CA 93106

We report on birefringence studies of entangled polystyrene solutions subjected to step changes of shear rate in a concentric cylinder Couette device. We consider four different flow histories: startup; double-step from one positive shear rate to another; reversing flows from a positive to a "negative" shear rate; and relaxation from steady flow to rest. Two different polymer concentrations are studied, corresponding respectively to ten and twenty entanglements per chain but with the molecular weight held fixed. Comparisons with theoretical calculations based on reptation models and simple approximations of such models highlight the role of flow-induced changes of the relaxation times for the different strain rate histories and also elucidate the effect of transient polymer chain stretching.

Monday 11:00 Los Angeles SC4

POLYELECTROLYTE SOLUTION RHEOLOGY

Ralph H. Colby[1], Wendy E. Krause[2], David C. Boris[3], and Julia S. Tan[4]
[1]Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802; [2]Chemistry, Pennsylvania State University, University Park, PA 16802; [3]Melt Sciences Laboratory, Eastman Kodak Company, Rochester, NY 14650; [4]Imaging Research and Advanced Development, Eastman Kodak Company, Rochester, NY 14650

We report oscillatory shear and steady shear data on aqueous solutions of polyelectrolytes with and without added salt. Two species of polyelectrolytes were studied. NaPSS is the sodium salt of poly(styrene sulfonate), a hydrophobic PE, and NaPAMS is the sodium salt of poly(2-acrylamido-2-methylpropane sulfonate), a more hydrophilic PE. The longest relaxation time is the product of terminal viscosity and recoverable compliance. This relaxation time is significantly longer than the relaxation time for shear thinning of the apparent viscosity in steady shear, as anticipated by the Rouse model. Rouse dynamics qualitatively describe the rheology of PE solutions over a wide range of concentration because the coil size rapidly decreases as the PE is concentrated, delaying the onset of entanglement effects. The chain length dependence of the entanglement concentration will be discussed in detail.

Monday 11:25 Los Angeles SC5

SCALING THEORY OF HYDROPHOBICALLY MODIFIED POLYELECTROLYTES.

Michael Rubinstein and Andrey V. Dobrynin
Chemistry, University of North Carolina, Chapel Hill, NC 27599

We present a scaling model of hydrophobically modified polyelectrolytes. In a dilute salt-free solution these polymers have a necklace-like shape with beads of flower-like micelles which have a hydrophobic core and charged coronas, connected by polyelectrolyte strings containing free hydrophobes. The aggregation number of micelles is proportional to the ratio of hydrophobic to electrostatic interaction. This necklace-like structure manifest itself in the unique scaling laws in the semidilute regime where the correlation length of a solution is of the order of the string length between two neighboring beads. For this polymer concentration range the viscosity of a solution is concentration independent in both entangled and unentangled regimes. We calculated the phase diagram of a system as a function of polymer and salt concentration and determined the rheological properties in different concentration regimes.

Monday Afternoon

Symposium NP
Polymers with Novel Architectures

Organizers: Patrick T. Mather and Michael Mackay

Monday 1:30 San Carlos I NP6

EFFECTS OF MICROSCOPIC AND MACROSCOPIC ARCHITECTURE ON THE GELATION AND VITRIFICATION OF THERMOSET RESINS

Jakob Lange[1], Peter J. Halley[2], Camilla T. Kelly[2], and Nara Altmann[2]
[1]Nestle Research Centre, Nestle, Lausanne, Switzerland; [2]Department of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

The effects of monomer architecture and fillers on the gelation and vitrification of thermoset materials has been measured. Specifically this paper investigates the gelation of methacrylate resins with various initial molecular architectures and functionalities, and also examines the effects of filler content on the vitrification of a model epoxy system. The chainwise crosslinking polymerisation of methacrylate resins with methacrylate, dimethacrylate and hyperbranched methacrylate groups was quanitified by dynamic rheology. The gel time was found to decrease with increasing functionality. Power law relaxation behaviour was observed at the gel point in all systems. The value of the power law exponent at gelation increased with increasing functionality at temperatures above the ultimate Tg, suggesting hydrodynamic screening effects were dominating effects of different fractal dimiension. The power law exponent below the ultimate Tg was lower and this was attributed to the influence of vitrification. The effect of fillers on the vitrification and ultimate Tg of a model epoxy system has been quantified by rheological analysis and differential scanning calorimtery (DSC). The influence of filler content on these transition will be correlated to effects on cure chemistry and physical properties.

Monday 1:55 San Carlos I NP7

BULK RHEOLOGY OF ETHYLENEDIAMINE (EDA)-CORE POLYAMIDOAMINE (PAMAM) DENDRIMERS

Srinivas Uppuluri[1], Faith A. Morrison[2], and Petar R. Dvornic[1]
[1]Michigan Molecular Institute, Midland, MI 48640; [2]Department of Chemical Engineering, Michigan Technological University, Houghton, MI 49931

Dendrimers are globular, nanoscopic macromolecules which as a result of their geometrically progressive growth patterns can reach high molecular weights while still retaining low polydispersity. Because of their precise structure, dendrimers are drastically different from other traditional macromolecules. Among these differences, two important ones are: (1) dendrimers are considerably more compact than their conventional open-ended linear counterparts, and (2) they have an extremely large density of molecular end-group functionality, which can reach to several thousands of end-groups per molecule.

The steady shear and linear-viscoelastic rheological properties of EDA-core, PAMAM dendrimers in bulk have been investigated as a function of generation (i.e., molecular weight). Generations 0-3 (M=517-6,909) exhibit constant shear viscosity, and G', G" were found to fit the single-mode Maxwell model with common modulus equal to 9.2×10^5Pa and relaxation times which vary as M^3. For generations 4-6 (M= 14,215, 28,826, 58,048) a constant viscosity was again found, and G' and G" fit the Rouse model with 2, 3 and 15 modes, respectively. These results are consistent with a picture of dendrimer dynamics in which the generation 0 dendrimer is a collapsed molecule

dominated by intramolecular H-bonding. Successively higher generations increase in size and in intermolecular H-bonding resulting in an increase in viscosity and relaxation time. When the outer shell of the dendrimer becomes crowded (i.e., when it begins to close upon itself above a critical degree of branching), the relaxation modes of individual dendron arms become visible. These results support a dense-shell/soft-interior model of dendrimer intramolecular morphology in the bulk.

Monday 2:20 San Carlos I NP8

A NEW TRANSIENT NETWORK MODEL APPLIED TO GUAR GUM

Roland H W. Wientjes, Michel H G Duits, Rob J J. Jongschaap, and Jorrit Mellema
Department of Applied Physics, University of Twente, Rheology Group, Enschede 7500 AE, Netherlands

We have studied the linear viscoelastic behaviour of monodisperse guar gum solutions. Guar gum is a linear polymer, which forms a transient network via interchain bonds when solved into water. In the frequency domain, we observed two plateau regimes for the storage modulus, separated by a broad transition regime. The temperature dependence of the regimes was different and allowed us to extract information about the energies associated with the bonds.

In the past several models have been developed to describe the linear behaviour of associative polymer solutions, but none of them can explain the mentioned phenomena. Inspired by the Lodge model, where each polymer chain is described as two sticky points connected by a spring we have developed a new model. Here the number of spring segments per chain is increased to seven with the connectivity of the chain taken into account. Many different chain states are possible from a completely free chain to a chain with all sticky points connected to the network. Transitions between these states are described by kinetic equations in which activation energies for creation and annihilation processes apear. Also the tube idea of the model of Doi and Edwards was used which precludes lateral motion. The loss of tension (essential for the relaxation spectra) is governed by the formation of new loose ends.

With this new model several types of relaxation spectra can be obtained: Several plateaus for the storage modulus are possible and time temperature superposition may or may not be satisfied. Since the model is capable of predicting our experimental observations but other behaviour as well it seems a promising model for the description of transient network systems.

Monday 2:45 San Carlos I NP9

NON-LINEAR RELAXATION DYNAMICS OF MULTI-ARM POLYMERS

Mohammad T. Islam and Lynden A. Archer
Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122

We describe the effect of an internal branch point on nonlinear relaxation dynamics of various multi-arm entangled polybutadiene molecules of the general type A3-(A)-A3. In low-amplitude oscillatory shear flow multi-arm polymers display broader relaxation spectra than linear polybutadienes of comparable molecular weight. Dramatic slowing down of cross-bar (A) relaxation by the entangled arms A is believed to be the source of this behavior. In nonlinear step strain experiments the A arms have a rather remarkable effect on polymer dynamics. At a critical shear strain γ around 6.0 ($<|E.u|> = 3.2$), the non-linear relaxation modulus $G(t; \gamma)$ abruptly decreases in value but retains similar time-dependence to $G(t; \gamma)$ at strains below the critical value. The drop in $G(t; \gamma)$ is reflected in the damping function and appears to be a consequence of arm withdrawal into the tube confining the cross-bar. This behavior is in near perfect agreement with a recent theoretical proposal for branched polymer dynamics. That this proposal is based on the notion of tensile forces on individual macromolecules due to mean-field tube confinement, supports the existence of such forces and provides convincing circumstantial evidence for the existence of such a tube. For all multi-arm polymers studied we also find time-strain separability at all strains with a separability time that appears insensitive to the arm withdrawal process.

Monday 3:35 San Carlos I NP10

A NOVEL PROCESSING AID FOR POLYMER EXTRUSION: RHEOLOGY AND PROCESSING OF POLYETHYLENE AND HYPERBRANCHED BLENDS

Ye Hong[1], Justin J. Cooper-White[1], Michael E. Mackay[1], Craig J. Hawker[2], Eva Malmstrom[3], and Nicola Rehnberg[4]

[1]Department of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia; [2]IBM Almaden Research Laboratory, San Jose, CA; [3]Royal Institute of Technology, Stolkholm, Sweden; [4]Application Technology, Perstorp Specialty Chemicals, Perstop, Sweden

Hyperbranch polymers (HBPs) belong to the same unique class of polymers as dendritic polymers, both being characterized by a highly branched, three-dimensional structure. However, unlike dendritic polymers, HBPs can easily be produced in industrial quantities at low cost, and yet still exhibit the fascinating properties previously reported for dendritic polymers. For this reason alone, they show great promise in a variety of applications.

The use of HBPs as a possible processing aid for linear low density polyethylene (LLDPE) was investigated. Blends of up to 10% HBP content were mixed via extrusion at 170°C to produce 1 mm diameter fibres. Processability, surface appearance and the rheological properties of the blends were evaluated. Surface analysis using the XPS technique was performed showing that the HBP had a preference to accumulate at the fibre surface. Melt fracture and sharkskin of the blends was successfully eliminated, and no preprocessing time was required. The power requirement for extrusion was decreased significantly as a result of reduced blend viscosity, and yet, the mass flow rate was greater than that of virgin LLDPE. Blends of LLDPE and paraffin wax were also studied. The surface appearance of HBPs/LLDPE blends was superior to those blends mixed with paraffin wax, as was the extruder performance. These results suggest that HBPs could function as a processing aid for LLDPE.

Monday 4:00 San Carlos I NP11

THE RHEOLOGY OF GEL PHASES OF ASSOCIATING POLYMERS IN THE PHASE SEPARATION REGIME

Giyoong Tae[1], Julia A. Kornfield[1], and Jeffrey A. Hubbell[2]

[1]Chemical Engineering, Caltech, Pasadena, CA 91125; [2]Biomedical Engineering, Swiss Federal Institue of Technology, Zurich CH-8044, Switzerland

Model "associative thickeners" can be made from a long, water soluble midblock(polyethyleneglycol, PEG) terminated at both ends by a hydrophobic block (typically a short alkyl segment, but have a fluoroalkyl segment). Relative to more extensively studied alkyl-terminated PEG, the fluoroalkyl capped chains are of interest because of the stronger hydrophobicity and consequently stronger association of $-C_nF_{2n+1}$ compared to $-C_nH_{2n+1}$. First, we characterize the phase behavior of the chain of associating polymer; the effect of PEG length and hydrophobe length on the equilibrium composition of coexisting sol and gel, using PEGs of molecular weight of 6K,10K, and 20Kg/mol with $-C_nF_{2n+1}$, n = 8 or 10. Next we examine the linear viscoelasticity of the gel phase as a function of M_{PEG}, n, and concentration. Like hydrocarbon terminated PEG, these systems show single relaxation behavior. The dependency of the relaxation time on M_{PEG} and concentration are similar to hydrocarbon-ended PEG.

Monday 4:25 San Carlos I NP12

DYNAMICS AND RHEOLOGY OF HAIRY ROD POLYMERS

Dimitris Vlassopoulos[1], G. Petekidis[1], G. Fytas[1], R. Rulkens[2], and G. Wegner[2]

[1]Institute of Electronic Structure and Laser, FO.R.T.H., Crete, Greece; [2]Max-Planck Institut für Polymerforschung, Mainz, Germany

Hairy-rod polymers represent a class of semiflexible polymers with important applications in particular thin films and mesoscopic structures in the photonics and electronics industry. In order to control the phase state and dynamics of these anisotropic macromolecules, it is essential to understand the coupling of translational to rotational diffusion. In this paper, we present a detailed investigation of the orientation dynamics of isotropic solutions of model hairy-rod poly (p-phenylenes) using a combination of dynamic light scattering and shear rheology. No nematic order was observed, and thus measurements of the orientation correlations in the isotropic regime extended in a wide

concentration range (0.5 < c/c* < 1400) and different solvents. Two relaxation processes were detected, which are of molecular origin and exhibit distinct characteristics. Both of them slow down very sharply with concentration, in an analogous fashion to the corresponding drastic increase of viscosity. With the support of dynamic rheological measurements, the fast process is attributed to orientation fluctuations of Kuhn segments whereas the slow one is proposed to relate to orientation correlations in space due to local ordering of parts of the molecules. As the concentration increases the formation of aggregates can be detected as extra relaxation process in the scattered intensity correlation function as well as in the low frequency viscoelastic moduli.

Monday 4:50 San Carlos I NP13

PREPARATIONS OF INTERPENETRATING POLYMER NETWORKS FOR IMPROVED CELLULOSE ESTER PLASTICS

Shih-Wei Ho[1], W. E. Skip Rochefort[1], James B. Wilson[2], and Stephen S. Kelley[3]
[1]Chemical Engineering Department, Oregon State University, Corvallis, OR 97331; [2]Forest Products Department, Oregon State University, Corvallis, OR 97331; [3]Center for Renewable Chemical Technologies and Materials, National Renewable Energy Laboratory, Golden, CO 80401

A series of semi-interpenetrating polymer networks (semi-IPNs) based on cellulose acetate butyrate (CAB) and novolac resins (NOV) was prepared. The goal of this work was to develop an understanding of how the type and frequency of chemical bonds affect the stiffness and creep resistance of cellulose ester plastics. The IPNs were prepared by the addition of hexamethylenetetramine (HEXA) curing agent to a CAB / NOV blend. The HEXA acts as a crosslinker for the novolac resin, thus creating the IPN. In the initial studies, CAB (number averaged MW: Mn = 70,000) blended with NOV (Mn = 900-1,000; weight averaged MW: Mw = 5,000-10,000) and various amounts of the HEXA crosslinker were studied. The blends were characterize d using rheological (Bohlin CS-50) and thermal (Shimadzu DSC) techniques.

As expected, the blends with higher HEXA content exhibited higher dynamic moduli (G', G''), viscosities and glass transition temperatures than the uncrosslinked polymers (CAB / NOV blends). It is anticipated that the IPNs will retain the good mechanical properties of cellulose acetate butyrate and will show higher creep resistance and stiffness. The mechanical characteristics will be measured using Dynamic Mechanical Analysis (Rheometrics RSA-II) and standard ASTM tests. The results will be analyzed to relate the degree of crosslinking in the IPN to the resultant enhancement in mechanical properties.

Symposium GN
General Session

Organizer: Wesley R. Burghardt

Monday 1:30 San Carlos III GN6

IS THE BEAD-SPRING DESCRIPTION APPLICABLE TO UNENTANGLED POLYSTYRENE MELTS ?

Ravi K. Verma and Julia A. Kornfield
Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

We have used rheooptical methods to study polymer melt dynamics for a series of unentangled and entangled polystyrene fractions, focusing on the validity of the Rouse model[i] for unentangled fractions. The stress optic rule is verified (birefringence and stress are out of phase, and the stress optic ratio C_r is independent of frequency) at frequencies much lower than that associated with the dynamic glass transition (i.e. in the terminal region for all fractions, and also in most of the plateau region for well entangled fractions). However, the temperature derivative of the stress optic ratio is positive for unentangled ($M < M_e$) fractions, which is in discord with the Rouse model. The T^{-1} scaling of C_r (expected for Rouse liquids) is observed only for well entangled fractions (when $M\ M_C$). Therefore, we conclude that the dynamic response is dominated by more local physics, which are not captured by the bead-spring description. Our conclusion is in accord with the work of Lodge and coworkers[i,ii], who estimate the size of each 'spring' in the model representation of a polystyrene chain to be ca. 5000 g/mol. The number of beads in unentangled polystyrene fractions ($M < M_e \sim 19000$ g/mol) would be inadequate for the applicability of the Rouse model.

i. The state of current literature is summarized by Lodge, T. P., Rotstein, N. A.; & Prager, S. *Adv. Chem. Phys.* **1990,** 1.
ii. Amelar, S.; Eastman, C. E.; Lodge, T. P.; & von Meerwall, E. D. *J. Non-Crystalline Solids*, **1991,** 132, 551.

Monday 1:55 San Carlos III GN7

DYNAMICS OF DISORDERED BINARY BLOCK COPOLYMER BLENDS

Ramanan Krishnamoorti and Soni Rai
Department of Chemical Engineering, University of Houston, Houston, TX 77204-4792

We have recently investigated the phase behavior of binary blends of block copolymers consiting of a symmetrical and a highly asymmetrical block copolymer of polystyrene and polyisoprene. Experimentally significant deviations from the prediction of the order-disorder transition by mean-field and self-consistent field theories were observed. These blends in their disordered state provide an excellent model system to investigate the role of large concentration fluctuations on the dynamics of the blend in the disordered state. As expected, the principle of time-temperature superposition fails for these blends. However, the effect of blending on the chain dynamics results in an unusual behavior -- the longest relaxation time of the long entangled sphere forming diblock accelerates with the addition of the short diblock much slower than that predicted by simple models, while the relaxation time corresponding to the concentration fluctuations accelerates exponentially with the addition of the short diblock. These results are discussed in terms of a simple phenomenological model that is consistent with the structure of these materials as elucidated by small angle neutron scattering.

Monday 2:20 San Carlos III GN8

COMPONENT FRICTION FACTORS IN STYRENE/ISOPRENE MIXTURES

Jodi M. Milhaupt and Timothy P. Lodge
Chemistry, University of Minnesota, Minneapolis, MN 55455-0431

The rheological properties of polymer liquids are strongly influenced by the rate of local segmental rearrangements, often described in terms of the monomeric friction factor. In particular, the temperature dependence of the viscosity and diffusivity are largely determined by the temperature dependence of the monomeric friction factor, which in turn depends on both the distance from the glass transition temperature and on the chemical structure. In polymer mixtures, each component friction factor may have a distinct temperature dependence, and a composition dependence that is so far impossible to predict. Consequently, accurate prediction of the rheological properties of polymer blends and copolymers on the basis of the component properties is difficult. We have developed a method to probe this composition dependence in immiscible systems, such as polystyrene/polyisoprene, and determined the temperature and composition dependence of the component friction factors over the complete range of composition. The results are remarkably simple, in contrast to those found in several miscible polymer blends.

Monday 2:45 San Carlos III GN9

SEGMENTAL FRICTION IN POLYMER DYNAMICS OF ENTANGLED SOLUTIONS AND MELTS

Xiaoping Yang and Shi-Qing Wang
Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Dynamics of entangled polymer solutions are studied in terms of concentration, temperature, solvent structure and molecular weight dependence of the Rouse segmental friction coefficient. It is well known that this monomeric friction constant dictates the temperature dependence of molecular relaxation and diffusion. A phenomenological treatment, incorporating the effective glass transition temperature of the solutions, is proposed to describe the observed viscoelastic behavior including invariance of the overall molecular relaxation time with concentration (i.e., polymer volume fraction f) at a specific temperature. Tube diameter a prescribed in the reptation theory for chain dynamics is measured to scale with f as $f^{-2/3}$ from f=0.3 to 1.0, and the predicted scaling for the plateau modulus G_0,

as $f^{7/3}$, agrees with experiment. Our approach offers a promising protocol for predicting dynamic and rheological properties of miscible polymer blends.

#: A short communication has been submitted in May, 1998 to Phys. Rev. Lett.

Monday 3:35 San Carlos III GN10

SIMPLE MOVING AVERAGE FORMULAE FOR THE DIRECT RECOVERY OF THE RELAXATION SPECTRUM

A. Russell Davies[1] and Robert S. Anderssen[2]
[1]Department of Mathematics, University of Wales - Aberystwyth, Aberystwyth, Ceredigion SY23 3BZ, United Kingdom; [2]Mathematical and Information Sciences, CSIRO, Canberra, ACT 2601, Australia

Different software packages are available commercially which can be applied to oscillatory shear data to recover an estimate of the relaxation spectrum of the viscoelastic material tested. The underlying algorithms, based on some form of regularization, are indirect and technically involved. The purpose of this paper is to present explicit moving average formulae which experimentalists can apply simply and directly to appropriately sampled oscillatory shear data. An estimate of the relaxation spectrum is recovered in seconds, from data with realistic levels of noise. The derivation of the moving average formulae is based on the recent theory of sampling localization [A.R.Davies and R.S.Anderssen, J. Non-Newtonian Fluid Mech., 73 (1997) 163-179]. This will be described only briefly. The main discussion will be centred around practical issues, such as resolution versus noise amplification; finite frequency sampling (limited range) and partially recoverable spectra; and the role of the natural duality between the storage and loss moduli in recovering the relaxation spectrum.

Monday 4:00 San Carlos III GN11

NONLINEAR VISCOELASTICITY OF CHEESE

Salman Tariq[1], A. Jeffrey Giacomin[1], and Sundaram Gunasekaran[2]
[1]Dept. of Mech. Engr. & Rheology Research Ctr., University of Wisconsin-Madison, Madison, Wisconsin 53706-1572; [2]Biological Systems Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706

Cheese viscoelasticity is commonly measured using uniaxial compression, uniaxial extension, creep, and stress relaxation. In shear, viscoelastic properties for many cheeses have been measured using small amplitude oscillatory shear. However, there is little on the measurement of nonlinear viscoelastic properties.

In this work, the nonlinear viscoelasticity of four cheese varieties was studied using large amplitude oscillatory shear (LAOS). The instrument used was a sliding plate rheometer incorporating a shear stress transducer [1]. The data were evaluated using spectral analysis, and results are presented in the form of shear stress *versus* shear rate loops. The effects of temperature, age, and fat content are discussed, and comparisons are made to the Lodge rubberlike liquid theory to establish the amount of nonlinearity.

[1] Giacomin, A.J., T. Samurkas, and J.M. Dealy, "A Novel Sliding Plate Rheometer for Molten Plastics," Polymer Engineering and Science, 29(8), 499-504 (April 1989).

Monday 4:25 San Carlos III GN12

TROTTERS IN EXERCISE: THE ROLE OF RHEOLOGY, SEDIMENTATION AND HEOLYSIS

Lawrence C. Cerny and Elaine R. Cerny
Cernyland of Utica, Huber Hts, OH 45424-3467

Trotter: A horse whose gait consists of the legs lifting in alternating diagonal pairs. The normal race is a mile in length traversed in about two minutes. The trotter is pulling a sulki (a light two-wheeled carriage having a seat for only one person) and his driver. The data to be reported here was taken before and after the race. The measurements that were taken were the following: The non-Newtonian hemorheology, the erythrocyte sedimentation rate and the malonamid kinetic hemolysis. Post-exercise values of the heatocrit (the red cell volume) were significantly higher

than those of pre-exercise. The yield stress values as calculated from the Casson equation were also increased but not directly related to the hematocrit changes. The sedigraphs were determined with an automatic sedimentimeter. The half-life of the sedimentation process increased after the exercise routine. Finally, the cells became slightly more fragile post-exercise.

Monday 4:50 San Carlos III GN13

VIEWING ENTANGLEMENTS AS A TWO PHASE SYSTEM IN POLYMER MATERIALS

J P. Ibar

EKNET Research, New Canaan, CT 06840

We present the results of an extensive investigation of the deformation behavior of an amorphous polymer, polycarbonate, and explain the results in terms of interactive coupling between conformers belonging to interpenetrating coil-macromolecules. Our investigation of the deformational properties includes viscous behavior (both capillar and Dynamic shear viscosity), stress-strain tensile tests at various rates and temperatures, flexural dynamic data below Tg, for both quenched and aged PC, and PVT results from 1.42 Tg (K) down to room temperature. All the results are consistent with a picture of the amorphous state suggested by the EKNET model [1] in which coiled macromolecules pack and interpenetrated when interacting with one another, to create and interactive phase which, in many respects, behaves like a blended phase which has its own visco-elastic characteristics. Newtonian and non_Newtonian viscosity behavior, PVT equation of state, and the effect of molecular wieght on these parameters can be quantitatively described with new formulas consistent with this two-phase approach. Furthermore, the mechanisms of toughening and embrittlement through physical aging can easily been described in terms of either the continuit or the segregation of the coil interfacial interactive phase, which defines "entanglements". Identical results on Polystyrene will also be evoked for comparion.

[1] J. P. Ibar, J. Macro. Mol. Sci.-rev., Macro. Chem. Phys., C27(3), 389 (1997).

Symposium EE
Extensional and Elongational Flow

Organizers: David James and Gareth McKinley

Monday 1:30 San Carlos II EE6

THE FLOW OF A VISCOELASTIC FLUID IN THE STRETCHING FILAMENT RHEOMETER

Oliver G. Harlen

Applied Mathematics, University of Leeds, Leeds, West Yorkshire LS29 7EG, United Kingdom

The stretching filament rheometer is becoming widely established as a technique for measuring the transient extensional viscosity of viscoelastic liquids. Although designed to produce pure and uniform extensional flow, there can be significant amounts of shear during the early stages of deformation. In this paper we present numerical simulations that show how the initial shape of the sample affects the stress distribution within the filament, and hence the viscosity measurement. From this we discuss how the design of the rheometer and interpretation of the data can be optimized to reproduce the true extensional viscosity.

The calculations are compared to mesurements on a monodisperse polystyrene solution by McKinley and Speigelberg. Finally we present a simplified one-dimensional model for the later stages of deformation.

Monday 1:55 San Carlos II EE7

A ONE-DIMENSIONAL THEORY FOR EXTENSIONAL FLOW OF A VISCOELASTIC FILAMENT UNDER EXPONENTIAL STRETCHING

David O. Olagunju
Department of Mathematical Sciences, University of Delaware, Newark, DE 19702

We consider the extensional deformation of a viscoelastic filament between two coaxial discs in which the bottom plate is fixed and the top plate is pulled at an exponential rate. For slender axisymmetric filaments the governing equation is approximated by a one-dimensional model. It is assumed that inertia and gravity are negligible. The primary goal is to determine the nature of deformations in the central portion of the filament. In particular, to determine if the flow approaches ideal uniaxial elongation and to find out rheological properties that enhance or inhibit ideal uniaxial kinematics.

The model equations admit a solution corresponding to ideal uniaxial elongation. A linear stability analysis shows that this solution is unstable for Newtonian filaments and for Oldroyd-B fluids with Deborah number, De less than 0.5. For De greater than 0.5, linear theory is not conclusive but points towards stability. In order to resolve this case the non-linear model is solved using a finite difference scheme. The numerical solutions show that ideal uniaxial elongation is unstable for De less than or equal to 0.5 in agreement with linear theory. For De greater than 0.5, our calculations show that the deformations in the central part of the filament approach ideal uniaxial elongation as the Hencky strain increases.

Monday 2:20 San Carlos II EE8

ACCOMMODATION OF RADIALLY INHOMOGENEOUS REGIONS IN RADIALLY AVERAGED MELT SPINNING EQUATIONS

Grant M. Henson and Stephen E. Bechtel
Engineering Mechanics, Ohio State University, Columbus, OH 43210

In the melt spinning of polymer fibers, temperature varies significantly across the fiber radius. Thus, any temperature-dependent material properties, including rheological parameters and even the entire form of the constitutive equation, may vary across some cross sections. For example, the fiber typically solidifies from the outside in, with a length of fiber being solid on the outside but molten on the inside for a short distance before the fiber completely solidifies. The solid part of the cross section may behave rigidly or as an elastic solid, and the molten portion may behave as a Newtonian fluid. If radially averaged thin-filament momentum equations are to be derived correctly, some homogenization or averaging scheme must be employed. The stress in the fiber at or near solidification has been of practical interest because it can be correlated with spun fiber properties such as birefringence. Because the region of inhomogeneous material response occurs close to where the fiber is solidifying, any averaging scheme will influence the calculated stress near solidification; it is therefore vital to do the necessary averaging correctly if the ability of the model to predict stress at solidification is to be preserved. We examine several schemes to accommodate inhomogeneous material response within a set of averaged 1-D equations. Predictions of steady spinline behavior are then presented for the various schemes.

Monday 2:45 San Carlos II EE9

FLOW BIREFRINGENCE AND COMPUTATIONAL STUDIES OF A POLYSTYRENE BOGER FLUID IN AXISYMMETRIC STAGNATION FLOWS

Wesley R. Burghardt[1], Ji-Ming Li[1], Bin Yang[2], and Bamin Khomami[2]
[1]Department of Chemical Engineering, Northwestern University, Evanston, IL 60208;
[2]Department of Chemical Engineering, Washington University, St. Louis, MO 63130

Flow birefringence is a valuable tool in non-Newtonian fluid mechanics of concentrated polymer solutions and melts, in which ample evidence supports the validity of the stress-optical rule. At the same time, substantial experimental and computational effort has been spent studying the rheology and fluid mechanics of dilute solutions, frequently in the form of Boger fluids. We are motivated by the question of whether birefringence can play a productive role in studying this type of fluid. Here we report a combined birefringence/computational study of a polystyrene-based Boger fluid in axisymmetric stagnation flows of the type previously studied in our groups using a concentrated polystyrene solution [JNNFM, Vol. 74, pp. 151 - 193 (1998)]. The fluid is formulated using a concentrated but unentangled polystyrene solution as the "solvent", and was subjected to both shear and extensional rheometry. Although both "polymer" and "solvent" stresses should be generated by polystyrene in this formulation, there are numerous reasons to anticipate failure of the stress-optical rule, even in shear flow. Somewhat surprisingly, steady and transient data support the validity of the stress optical rule in shear for this solution up to fairly high Weissenberg number. In complex, mixed shear/extensional flows, validity of the stress-optical rule becomes even more highly questionable for dilute solutions. We compare birefringence distributions with calculations based on Giesekus and FENE-P constitutive models. The FENE-P model is the simplest molecular model which is capable of independent prediction of stresses and birefringence in situations in which the stress-optical rule should fail (in this case owing to finite extensibility). We explore the extent to which an "enlightened" comparison between computation and birefringence, in which the stress-optical rule is abandoned, leads to satisfying results. Such an exercise serves as a prototype for similar comparisons based on more sophisticated molecular models.

Monday 3:35 San Carlos II EE10

BROWNIAN DYNAMICS SIMULATIONS OF DILUTE POLYSTYRENE SOLUTIONS

Lei Li[1], Ronald G. Larson[1], Tam Sridhar[2], and D. A. Nguyen[2]
[1]Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136; [2]Chemical Engineering, Monash University, Clayton, Victoria 3168, Australia

This paper builds on recent Brownian dynamics simulations of extensional flow of DNA solutions, which show that the configurational dynamics of individual, long, DNA molecules can be accurately simulated by Brownian dynamics simulations using conventional bead-spring chains with finite extensibility, as long as the molecular characteristics, including extensibility and drag coeffcients, are properly modeled. The agreement achieved in the DNA simulations suggest that for dilute enough solutions, there are no serious gaps in our understanding of the basic physics of polymer stretching behavior in extensional flows. However, for DNA, there are no stress measurements available. Therefore, in this talk, the methods that proved successful for individual DNA molecules are applied to well characterized dilute solutions of polystyrene (i.e., Boger fluids) in extensional flows generated by the filament stretching device. Using known parameters of polystyrene molecules, and assuming near-theta solvent conditions, the stretching behavior and stress generated by large ensembles of simulated molecules are compared to the stress measured experimentally. Discrepancies between experiment and simulations will be discussed, along with their possible causes.

Monday 4:00 San Carlos II EE11

PROBING THE COIL-STRETCH-COIL PROCESS IN ELONGATIONAL FLOW OF DILUTE POLYMER SOLUTIONS

John M. Wiest
Chemical Engineering, University of Alabama, Tuscaloosa, AL 35487

Dilute polymer solutions exhibit their most striking properties in extensional flows, because these flows can distort the molecules substantially. One of the most controversial theoretical results regarding extensional flows of dilute solutions regards the presence or absence of coil-stretch transitions. However, the development of filament stretching devices with relatively clean extensional kinematics now allows the testing of many theoretical predictions regarding these transitions. These devices also allow examination of the processes by which the molecules relax upon cessation of the flow. Here we use a bead-spring chain model with finitely extensible springs to probe these processes. We find that the process by which the molecules relax is substantially different from that by which they stretch, and we probe the relaxtion process by examining multiple elongation relaxation steps.

Monday 4:25 San Carlos II EE12

STRESS-BIREFRINGENCE HYSTERESIS IN EXTENSIONAL FLOWS OF DILUTE POLYMERIC SOLUTIONS: THE EFFECT OF HYDRODYNAMIC INTERACTION

Indranil Ghosh[1], Robert A. Brown[1], Robert C. Armstrong[1], and Gareth H. McKinley[2]
[1]Chemical Engineering, M.I.T., Cambridge, MA 02139; [2]Dept. of Mechanical Engineering, M.I.T., Cambridge, MA 02139

Experiments conducted with a filament stretching rheometer (McKinley et al) have demonstrated important phenomena, such as stress-birefringence hysteresis and the breakdown of the stress optical law. (Doyle et al) have pointed out that the FENE dumbbell model underpredicts the extent of stress-birefringence hysteresis. However, this model does not account for the internal degrees of freedom in a polymer chain or hydrodynamic interactions (HI) between chain segments. We investigate the importance of these effects on the unraveling of a chain during the start-up and relaxation of a uniaxial extensional flow. FENE chains, both with and without HI, are simulated using Brownian Dynamics. HI is incorporated through the Rotne-Prager-Yamakawa (RPY) tensor. Our findings show that when drag is distributed along the backbone of the molecule in a multi-bead FENE chain (about 20 beads), the elongational viscosity and birefringence are reduced at all times during a transient extensional flow. Thus, the extent of the hysteresis is actually decreased. Introducing HI into the FENE chain model reduces the rate of stress growth, and most surprisingly, for strains large enough to allow stress saturation, the inclusion of HI has little effect on the stress-birefringence plots. Since the use of multi-bead-spring chains with HI does not improve the agreement between simulation and experiment, we believe that new methods for modeling drag and HI on a polymer chain are required. We discuss some alternative approaches.

Monday 4:50 San Carlos II EE13

QUANTIFICATION OF ENTANGLED POLYMER BEHAVIOR IN SHEAR AND UNIAXIAL ELONGATIONAL FLOWS

Michael K. Lyon[1], Cattelaya Pattamaprom[2], Ronald G. Larson[2], and David W. Mead[1]
[1]Department of Mech. Eng. and Appl Mech., University of Michigan, Ann Arbor, MI 48109;
[2]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109

The nonlinear response of monodisperse and polydisperse concentrated polystyrene solutions subjected to transient simple shear and uniaxial elongational flows has been investigated experimentally and theoretically. Predictions utilizing a recently developed molecular model that includes nongaussian chain stretching, polydispersity, diffusive and convective constraint release, and fluctuational motion of the polymer molecules [1], without introducing any free parameters to the original Doi-Edwards theory [2] are compared to experimental data acquired from Rheometrics Aries and Melt Elongational rheometers. Of particular interest is the applicability of this new model in providing quantitative predictions for the nonlinear behavior of well entangled solutions and melts subjected to well defined flow fields.

[1] Mead, D.W., Larson, R.G., Doi, M. in preparation.
[2] Doi, M., Edwards, S.F., "The Theory of Polymer Dynamics," Oxford University Press Inc., New York, NY (1987).

Symposium SC
Solutions and Coating Rheology

Organizers: Eric S. G. Shaqfeh and L. E. "Skip" Scriven

Monday 1:30 Los Angeles SC6

SOLUTIONS OF ASSOCIATIVE POLYMERS

William B. Russel[1], Quynh T. Pham[1], Jack T. Thibeault[2], and Willie Lau[2]
[1]Chemical Engineering, Princeton University, Princeton, NJ 08544; [2]Research Laboratories, Rohm and Haas Company, Spring House, PA 19477

Hydrophobically modified water soluble polymers of linear triblock structure form associated solutions with enhanced viscosity and viscoelasticity relative to the unmodified polymer. For highly monodisperse poly(ethylene oxides) endcapped with alkane hydrophobes, we find three distinct regimes beyond the critical micelle concentration. At high dilution, the associative polymers form flowerlike micelles with both ends in a hydrophobic core surrounded by a corona of the looped backbones. With increasing concentration interactions between micelles permit exchange of end-blocks, which results in an entropic attraction. This drives a temperature-independent phase transition between the dilute micellar phase and a highly associated liquid phase. The dynamics of the "gas" phase and the phase transition can be correlated via the adhesive hard sphere model. The condensed phase exhibits a high frequency elastic modulus controlled by the compressibility of the corona and the extensibility of the bridging chains, while the dissociation kinetics govern the low shear viscosity. These systems display characteristics of both micellar solutions and classical reversible networks.

Monday 1:55 Los Angeles SC7

HIGH-SHEAR VISCOMETRY OF POLYMER SOLUTIONS

P. Dontula[1], L.E. Scriven[1], Christopher W. Macosko[1], R. Garritano[2], and P. Mode[2]
[1]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; [2]Rheometric Scientific, Inc., Piscataway, NJ

Coating flows contain localized regions where the liquid suffers intense shear and extension of short duration. In slot, slide and roll coating, shear rates can reach as high as 50,000 1/s; in blade coating, they can be an order of magnitude larger. The rheological response of liquids in such flows can be complex and drastically different from that with Newtonian liquids. Indeed, the onset of ribbing-like pattern in the forward-roll film-split is a more sensitive indicator of the presence of dilute polymer than are state-of-the-art measurements of shear and apparent extensional viscosity. Definitive measurements at high strain rates are also important to guide development of constitutive equations used to model coating flows. Shear viscosities of glycerin-water mixtures and aqueous polymer solutions at rates up to 200,000 1/s measured with a small-angle cone (0.001 rad) and plate will be presented. These will be compared with similar measurements reported in the literature with narrow-gap concentric cylinders and parallel-plate apparatus. The advantages and limitations, notably viscous heating, of rotational instruments versus pressure-gradient-driven flow through a narrow slit will be discussed.

Monday 2:20 Los Angeles SC8

ELASTIC INSTABILITIES IN FREE SURFACE DISPLACEMENT FLOWS

Alex G. Lee and Eric Shaqfeh
Department of Chemical Engineering, Stanford University, Stanford, CA 94305

Instabilities developing at the interface between two immiscible fluids can give rise to a rich set of fingering phenomena collectively known as Saffman-Taylor fingers. Although qualitative differences when compared to Newtonian fingering have been widely reported in experiments with viscoelastic fluids, the mechanisms for the observed changes in fingering pattern remain largely unknown. In an effort to achieve a better understanding of the role of elasticity on the stability of fluid-fluid interfaces, the Saffman-Taylor problem is investigated both experimentally and theoretically. The experimental set-up is a modification of that introduced by Rabaud in which a viscous fluid is placed in the narrow gap between two rotating cylinders. Through the experimental measurements, a correlation between the critical conditions for the onset of fingering and the intrinsic properties of the fluids is established for the first time. Other new elastic effects observed include: increase in onset wavenumber with increasing elasticity coefficient (Wi/Ca), reduction in film thickness in elastic fluids at low capillary and Weissenberg numbers, and the formation of cusps at the interface when only one of the two cylinders is rotated. To understand these effects we use DPIV to investigate the flow fields near the interfaces at both sub- and super-critical flow regimes. To complement these experiments a theoretical stability analysis is developed under the assumption of a long-wave instability, thus the details of the flow near the interfaces can be neglected and a modified version of the original averaged boundary conditions of Saffman & Taylor can be applied. The perturbation analysis performed with the Oldroyd-B model shows that due to a resonance effect, the growth rate for elastic fluids can increase sharply with increasing elasticity coefficient (Wi/Ca). This result may partially explain the strong destabilization and increase in critical wavenumber observed in our experiments for highly elastic fluids.

Monday 2:45 Los Angeles SC9

ROLE OF FLUID ELASTICITY AND DYNAMIC MODULATION ON STABILITY OF SINGLE AND MULTILAYER COATING FLOWS

C T. Huang and Bamin Khomami
Department of Chemical Engineering, Washington University, St. Louis, MO 63130

In this study we have theoretically investigated the effect of fluid elasticity and dynamic modulation on the stability of single and multilayer flows down an inclined plane by utilizing asymptotic analysis and spectral based numerical techniques. In absence of dynamic modulation, our results indicate that for slow multilayer flows down an inclined plane (i.e., stable free surface) a stable flow to longwave disturbances can only be obtained when the elasticity gradient is in opposite direction of the gravitational field (purley elastic) and viscosity gradient is in the direction of the gravitational field (purley viscous) provided the most viscous fluid is adjacent to the wall and the most elastic fluid is in the top layer. This is in contrast to multilayer channel flows where the depth ratio plays a significant role in determining the stability of the interface. Utilizing Flouqet theory, we have also shown that dynamic modulation can significantly affect the stability of single and multilayer inclined plane flows. Specifically, in presence of dynamic modulation flows that are otherwise unstable for extensive range of viscosity and elasticity ratios, can be stabilized or visa-versa. In particular, in a ceratin parameter range resonance between a free surface and an interface gives rise to extremely rich dynamics and early transition to chaos.

Symposium IR
Interfacial Rheology and Rheological Modifiers

Organizers: Shi-Qing Wang, Stuart Kurtz and Bob Mendelson

Monday 3:35 Los Angeles IR1

ISOTROPIC-NEMATIC TRANSITION IN A TWO-DIMENSIONAL POLYMER SOLUTION

Kang Sub Yim, Gerald G. Fuller, Curtis W. Frank, and Channing R. Robertson
Chemical Engineering, Stanford University, Stanford, CA 94305

The isotropic-nematic transition of liquid crystalline polymers in two dimensions is considered through studies of monolayer films at the air-water interface. UV absorption spectroscopy is used to determine molecular orientation on a poly-p-phenylene sulfonic acid (PPPSH) monolayer. A well-defined extensional flow is imposed in the monolayer to study the dynamics of flow-induced anisotropy. Pure PPPSH polymer monolayers are rigid and resistant to flow, therefore a matrix of stearic acid (SA) at moderate concentrations is added to this polymer solution to fluidize the film. The surface pressure-area analysis shows that this mixture of polymer and fatty acid is completely miscible, which is confirmed by Brewster angle microscopy. The UV dichroism data shows that isotropic-nematic transition occurred at the surface pressure 8 mN/m at 40 mol% PPPSH/SA mixture. Measurement of the surface modulus were also performed to verify this transition.

Monday 4:00 Los Angeles IR2

FRICTION PROPERTIES OF CONFINED FILMS OF CHAIN ALCOHOLS

Frieder G. Mugele, Leonnard Broekman, and Miquel Salmeron
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

We investigated thin films of undecanol using the Surface Forces Apparatus (SFA). Simultaneously with the interferometric thickness measurement, we recorded the dynamic friction coefficient and the capacitance across the contact area.

When the mica surfaces are approached, layering of the undecanol molecules is observed. The layering transitions are accompanied by distinct increases of the friction coefficient. The last monolayer displays two interesting features: (a) Upon compression (constant film thickness within 2A), two abrupt jumps of the friction coefficient are observed, each accompanied by a small increase in capacity. (b) Upon increasing the shear-amplitude beyond a critical value the friction coefficient suddenly drops. Both phenomena are interpreted in terms of structural transitions within the monolayer film.

Monday 4:25 Los Angeles IR3

SURFACE RHEOLOGICAL STUDY OF A POLYMERIZABLE PHOSPHOLIPID MONOLAYER

Carlton F. Brooks[1], Jochen Thiele[1], Gerald G. Fuller[1], Curtis W. Frank[1], Wolfgang Knoll[2], and David F. O' Brien[3]
[1]Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025; [2]Polymer Research Division, Max Planck Institute, Mainz 55021, Germany; [3]Department of Chemistry, University of Arizona, Tucson, AZ 85721

Phospholipids with polymerizable groups have found considerable interest as a method to increase the stability of organized films. Such films are of interest as novel supramolecular assemblies as well as models for biological systems. We have investigated the polymerization of monolayers of diene substituted phosphatidylcholines at the air-water interface to understand the molecular organization and interactions within these films. Lipids with one and two diene groups form linear and cross-linked polymers, respectively. The polymerization is performed by exposing the monolayer to UV light. Turning the lamp off allowed us to pause the reaction while measurements were made to monitor the progression of the polymerization. The dynamic surface moduli, G_s' and G_s'', were measured after different exposure times with a custom made surface rheometer. In this device, a magnetized rod situated at the interface is subjected to an oscillation force using a magnetic field. By measuring the displacement of the rod relative to the applied force, the surface modulus is calculated for a monolayer. The film morphology was observed with Brewster angle microscopy (BAM). When the unpolymerized film is compressed above a surface pressure of 18 mN/m, collapsed domain structures are observed with BAM. As the monomer is exposed to UV light in this collapsed state, the collapsed structures disappeared. The polymerized region shrinks to a higher density, allowing the collapsed structures to fall back into the monolayer plane. For the cross-linking polymer, an order of magnitude increase in the surface modulus was observed. Results from the polymerization of the linear polymer will also be presented.

Monday 4:50 Los Angeles IR4

THE NOVEL TECHNIQUE OF EXTRUSION OF PULP USING CARBOXY-METHYL-CELLULOSE (CMC): EFFECT OF CMC CHARACTERISRICS ON PULP RHEOLOGY.

Manish Giri[1], W. E. Skip Rochefort[1], and John Simonsen[2]
[1]Chemical Engineering, Oregon State University, Corvallis, OR 97330; [2]Forest Products Research Lab, Oregon State University, Corvallis, Oregon 97331

A novel technology for processing pulp slurries with high inorganic filler content and at high consistencies (solids content) is extrusion. Extrusion is a widely researched and implemented process. A substantial portion of this waste from pulp and paper industries is discarded. Using extruders similar to food extruders and consistencies ranging from 30-45%, profiles can be extruded from this waste into useful products. A critical factor in the successful extrusion of pulp slurries is the use of dispersants. In their absence of, the pulp fibers flocculate, separate from the water and subsequently surge out of the extruder. It has been shown that CMC has the ability to disperse the pulp fibers and promote inter-fiber bonding via its carboxy-methyl groups. Although CMC is an anionic polymer, it has the intrinsic ability to facilitate fiber dispersion and penetrate the fiber network thereby increasing the fiber surface availability for bonding. CMC reduces the frictional forces at the fiber contact points. This improves the rheological properties and makes pulp processing easier. We have been able to determine the effect of CMC molecular weight on the extrusion behavior of pulp. The torque drop experiments were characterized as macro-rheological since they measure the viscosity of the entire multi-phase system. The critical shear experiments in which, the pulp fiber-polymer network was subjected to a range of shear stress were characterized as micro-rheological because the response elicited from the fiber network when subjected to a shear field depended on the average strength of the fiber-fiber contact point. Adsorption isotherms were generated to understand the mechanism of torque reduction for each type of CMC. The bulk solution characteristics had little effect on our system. We also investigated the effect of ionic strength on the extrusion behavior of pulp and on the critical shear stress of the network. However, no significant relationship was obtained.

Tuesday Morning

Symposium PL
Plenary Lectures

Bingham Lecture

Tuesday 8:30 Steinbeck Forum PL2

NONLINEARITIES AND INSTABILITIES IN THE FLOW OF MOLTEN POLYMERS

John M. Dealy
Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada

Thirty years ago I became interested in the nonlinear viscoelasticity of molten polymers and since then have developed several rheometers for the study of nonlinear behavior. The most fruitful of these is a sliding plate rheometer incorporating a shear stress transducer, and the latest version of this instrument can be used to study the response of melts to large, rapid shearing deformations at 300 C and 10,000 psi. Nonlinear data are essential in the development of constitutive equations suitable for the simulation of industrial forming operations, and I initially anticipated that the nonlinear regime would also prove to be a phenomenologically rich field of observation. However, this did not turn out to be the case, because the melt always finds some way to avoid the large stresses that might produce exotic rheological behavior. The mechanisms deployed by the melt to deal with large, rapid deformations include wall slip, fracture, tearing, common-line motion, cavitation and various types of secondary flow. These phenomena were initially looked upon as experimental "problems", but it is now clear that they are essential aspects of the behavior of molten polymers. As such, they will provide a very rich field of study for many years to come. Meanwhile, it is my present belief that the linear viscoelastic regime provides the richest source of information on the molecular structure of thermoplastics. If they are of sufficiently high quality, such data can be used to infer the molecular weight distribution of linear polymers, and, when combined with other analytical data, they can indicate the degree of long chain branching.

Symposium VP
Viscoelastic Processing Flows: Theory and Experiment

Organizers: Albert Co and Bamin Khomami

Tuesday 9:45 San Carlos I VP1

STUDIES OF HIGH DEBORAH NUMBER FLOWS OF A POLYISOBUTYLENE IN A LONG DIE WITH SQUARE CROSS SECTION

Vyacheslav B. Birman[1], Arkady I. Leonov[1], and Joseph Padovan[2]
[1]Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301;
[2]Department of Mechanical Engineering, The University of Akron, Akron, Ohio 44325-0309

A large capacity set up of a RAM extruder type was built up to study high Deborah (De) number flows of polymers with De < 10,000. A new version of particle image velocimetry was developed to measure the velocity field. During the measurements, tracer particles were simultaneously illuminated by a focused laser beam and by a lamp, with only those particles traced that passed through the beam. This way of measurement allows one to find the location of a particle in the direction of optical axis of the lens which makes the particle image on the CCD detector of a video

camera. A device employing this method was designed and used to measure velocity profiles. The results of these measurements in two cross sections of square die at three values of pressure are presented. The velocity was defined as a ratio of displacement to the time during which this displacement occurred. The values of errors in measurements of coordinates and time were estimated as 20 microns and less than 0.1%, respectively. A large plateau in the axial velocity profile was found at a relatively small Deborah number, De = 145. In the flow with higher Deborah number, De = 3,900, almost flat axial velocity profiles were detected. The presence of cross-sectional components of velocity due to the geometrical complexity of the die was also detected. However, the attempts to measure them by this method did not lead to reliable results, since the values of these components were found about 1% of the magnitude of axial velocity.

Tuesday 10:10 San Carlos I VP2

EXPERIMENTAL INVESTIGATION OF VISCOELASTIC LID DRIVEN CAVITY FLOWS

Anne M. Grillet[1], Eric Shaqfeh[1], and Bamin Khomami[2]

[1]Dept. of Chemical Engineering, Stanford University, Stanford, CA 94022-5025; [2]Department of Chemical Engineering, Washington University, St. Louis, MO 63130

We have performed flow visualization and birefringence measurements of lid driven cavity flow of an elastic Boger fluid in order to better understand the purely elastic instabilities in recirculating flows which have been reported elaswhere in the literature [Grillet & Shaqfeh (1996), Pakdel & McKinley (1998)]. Full field velocity measurements are taken with a Dantec FlowMap PIV system and compared with published results by Pakdel et al (1997). Experimental flow birefringence is compared with numerical calculations of the polymer stress by Grillet & Shaqfeh (1996). We will discuss our results within the context of known mechanisms for purely elastic instabilites in Taylor-Couette and planar stagnation flows. Time permitting, these results will also be compared to fully elastic finite element simulations presented last year.

[1] A.M. Grillet and E.S.G. Shaqfeh. "Observations of viscoelastic instabilities in recirculation flows of Boger fluids." *J. Non-Newt. Fluid Mech.* **v64** (1996) p141-155.
[2] P. Pakdel and G.H. McKinley. "Cavity flows of elastic liquids: Purely elastic instabilites." *Phys. Fluids* **v10** #5 (1998) p1058-1070.
[3] P. Pakdel, S.H. Spiegelberg and G.H. McKinley. "Cavity flows of elastic liquids: Two-dimensional flows." *Phys. Fluids* **v9** #11 (1997) p3123-3140.

Tuesday 10:35 San Carlos I VP3

NUMERICAL SIMULATION OF FLOWS OF POLYMER SOLUTIONS AND MELTS THROUGH CONTRACTIONS

Evan Mitsoulis

Department of Mining Engineering and Metallurgy, National Technical University of Athens, Athens 157-80, Greece

Two problems are considered for numerical simulation with viscoelastic constitutive equations, with the objective to check their validity and ability to predict experimental data. One is flow of a polymer melt (LLDPE) through tapered capillary dies, while the other is flow of a model polymer solution (fluid S1) through an abrupt 4:1 contraction. The constitutive equation used is the factorized K-BKZ integral equation with multiple relaxation times [1]. For the case of flow of polymer melts through a tapered die, the numerical simulations show that there is no vortex activity. The emphasis is on determining the pressure losses in the system and compare them with data that have appeared previously in an experimental study [2]. The effect of different material parameters is examined, in particular the normal stresses as measured in shear and the assumed elongational viscosity. Comparisons with predictions from purely viscous simulations are also performed. For the case of flow of polymer solution S1 through an abrupt 4:1 contraction, the numerical simulations show that good agreement is obtained for the vortex growth when compared with recent experimental findings [3]. The high elongational viscosity of the fluid is found to be primarily responsible for the large and extended vortices appearing in the contraction reservoir.

[1] A.C. Papanastasiou, L.E. Scriven and C.W. Macosko, J. Rheol., 27, 387-410 (1983)
[2] S.G. Hatzikiriakos and E. Mitsoulis, Rheol. Acta, 35, 545-555 (1996)
[3] J.A. Byars, R.J. Binnington and D.V. Boger, J. Non-Newtonian Fluid Mech., 72, 219-235 (1997).

Tuesday 11:00 San Carlos I VP4

EXPERIMENTAL OBSERVATIONS AND 3-D NUMERICAL SIMULATIONS ON THE DEVELOPMENT OF SECONDARY FLOWS INDUCED BY THE SECOND NORMAL STRESS DIFFERENCE IN STRAIGHT CHANNELS

Benoit Debbaut[1] and Joseph Dooley[2]
[1]Polyflow s.a., Fluent Inc., Louvain-la-Neuve, Belgium; [2]Dow Chemical Company, Midland, MI 48640

The effect of second normal stress difference is analysed by observing the co-flow of two batches of the same viscoelastic fluid, each with a different pigmentation, in straight ducts with a square cross-section. The development of secondary flows is observed by tracking the motion of the interface between both fluid layers. Three-dimensional numerical simulations are also performed on the basis of a multi-mode differential viscoelastic fluid model and are compared with the experiments. A good agreement is found between the experimental observations and their numerical counterparts.

Tuesday 11:25 San Carlos I VP5

THREE DIMENSIONAL VISCOELASTIC ANALYSIS OF POLYMER MELT FLOW: MODELING AND VERIFICATION

Frank P. Baaijens, Jeroen F. Schoonen, Wilco M. Verbeeten, Arjen Bogaerds, Gerrit W. Peters, and Han E. Meijer
Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5600 MB, Netherlands

In recent years a number of researchers have demonstrated that in complex flows existing constitutive models, like the PTT and the Giesekus model, perform remarkably well in predicting observed stress fields in shear dominated flows, while an increasing mismatch with increasing Weissenberg number between experimental and computational stress fields is found in flow domains with strong elongational components . The basic reason for this is the inability of most existing models to independently control the elongational and shear properties with sufficient flexibility. Based on these results, a new class of Maxwell-type models is proposed in which the relaxation time and the modulus are functions of the first and second invariant of the extra stress tensor. These functions are chosen such that in the limit of infinitesimal deformations the Maxwell model is recovered. Furthermore, the product of the relaxation time and the shear modulus is fixed to faithfully represent the viscous behaviour in simple shear flow by either using the Ellis model or by invoking the Cox-Merz rule. By choosing the relaxation time according to existing models, like in the PTT model, models are obtained in which the planar and uni-axial elongational viscosities are to a large extend decoupled from the shear properties. To identify certain material parameters, and to access the predictive capabilities of these models, a number of flow geometries are investigated using FIB and LDA: flow past a confined cylinder, planar contraction and in a cross-slot device. In this way, combined shear-elongational flows are examined. Some of the geometries yield three dimensional flows, requiring special interpretation of the measured data. Results are obtained for both polymer solutions and melts, while computations are performed using a fully coupled three dimensional viscoelastic analyis using multiple relaxation times based on the DEVSS/DG formulation.

Symposium GN
General Session

Organizer: Wesley R. Burghardt

Tuesday 9:45 San Carlos III GN14

POLYPROPYLENE CRYSTALLIZATION AS PHYSICAL GELATION PROCESS

Natalia V. Pogodina, Sanaul Siddique, Jan van Egmond, and H. Henning Winter
Chemical Engineering, University of Massachusetts, Amherst, MA 01003

Polypropylene Crystallization as Physical Gelation Process Natalia V. Pogodina, Sanaul Siddique, Jan Van Egmond, H. Henning Winter Department of Chemical Engineering and Department of Polymer Science University of Massachusetts, Amherst MA 01003 (USA) Crystallization of isotactic polypropylene (iPP) at low supercooling is studied by Rheology, differential scanning calorimetry (DSC) and small angle light scattering (SALS). Rheology is very sensitive to the degree of molecular connectivity. Evolution of the dynamic moduli G', G" at early stages of crystallization is the same as in chemical gelation. The physical gel point is manifested in the power law behavior of the shear relaxation modulus $G(t) = St^{-n}$ (where S is the gel stiffness, n is the relaxation exponent). With an increase of supercooling n decreases, S increases; the gel time decreases exponentially. Crystallinity growth (determined by DSC) followed the Avrami model. Crystallization kinetics is governed by the characteristic ratio of gelation and Avrami time tc/tA . Gel point occurs in the time range 0.1< tc/tA < 0.3 for various supercooling. The degree of crystallinity of the critical gel as determined by rheology/DSC is less than 4%. This very low crystallinity suggests that the network is "loose" and the gel is soft. SALS patterns at the gel point show circular symmetry in both HV and VV modes, that suggests very low anisotropy of the growing aggregates. The evolution of 2-fold and 4-fold symmetry patterns at the latest times suggests that spherical superstructures are developed at the late stages of crystallization. The maximum in the density fluctuation (maximum in VV invariant) occurs very close to the gel point. It is physically reasonable, because the impingement of regularly packed spheres (model for scattering analysis) occurs when their volume fraction is 0.5. Growing aggregates are characterized by very low anisotropy and internal crystallinity and are of about 1 micron in radius.

Tuesday 10:10 San Carlos III GN15

EFFECT OF SOLVENT QUALITY ON THE GELATION OF KAPPA-CARRAGEENAN

Srividya Ramakrishnan and Robert K. Prud'homme
Chemical Engineering, Princeton University, Princeton, NJ 08544

The rheology and conformational transition of kappa-carrageenan in aqueous solutions of glycerol at low water activity is studied using optical rotary dispersion (ORD) and rheology. Carrageenan forms a hydrated gel in water but a weakly flocculated network of partially hydrated particles in glycerol. The melting transitions of carrageenan in glycerol/water solutions show a single peak in the complex moduli at low and high glycerol concentrations, and two peaks at approximately equal concentrations of glycerol and water. These are thought to be due to the breakage of hydrogen bonds (low temperature peak) and ion dissociation (high temperature peak). The helix coil transition is shifted to higher temperatures with increasing glycerol content. Comparison of the rheology and ORD curves reveals that gelation occurs through helix aggregation in water but the lower solubility of carrageenan results in a more random network of helices in glycerol.

Tuesday 10:35 San Carlos III GN16

POLAR ASSOCIATION IN POLYETHYLACRYLATE OBSERVED AT SMALL SHEAR AND LARGE ELONGATION: EFFECT OF CONCENTRATION OF POLAR SOLVENT

Nobuyuki Nakajima and Joseph Varkey
Institute of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

Polyethylacrylate is an elastomer, which exhibits strain-induced association in elongation, a behavior quite similar to strain-induced crystallization of crystallizable elastomers. The first question is whether or not the strain-induced

association is suppressed when the polymer is diluted with polar solvents. The second question is whether or not some extent of polar association is present even in the quiescent state and detected under small shear deformation.

The sample elastomer was a "gel-free" grade and the plasticizer was dibutyl phthalate. The polymer concentration was 100, 90, 85 and 80%. Dynamic mechanical measurements were performed in shear in the linear region of viscoelastic property. Elongational measurements were performed at four machine speeds.

The linearized elongation modulus-time curve was in good agreement with the shear modulus-time curve with a factor of 3, for 85 and 80% solution. This is similar to the cases for nonpolar elastomers. Therefore, at these concentrations there is no polar association.

For 100 and 90% solutions the elongational modulus curve was significantly higher than three times of the shear curve. This indicated that the strain-induced polar association did occur.

The rubbery plateau modulus observed in the shear measurements hardly changed from 100% to 90% polymer concentration. Upon further dilution it decreased as expected. This behavior is similar to that observed with polyvinyl chloride, which contains microcrystallites as physical crosslinks. Small addition of plasticizer sometimes facilitates crystallization, resulting the increase of modulus. This off-sets the decrease of modulus by dilution. In the present case the polar association appears to be acting as a physical crosslink and small addition of plasticizer is enhancing the association. When the polymer is diluted beyond 90% there is no indication of the association under both strained and unstrained condition.

Tuesday 11:00 San Carlos III GN17

VISCOELASTIC PROPERTIES OF POLYURETHANE ELASTOMERS

Sachin Velankar and Stuart Cooper
Dept. of Chemical Engineering, University of Delaware, Newark, DE 19716

Polyurethanes are microphase-separated multiblock copolymers that have found numerous applications as elastomers and coatings. Rheological studies of polyurethane melts have been hindered by the fact that thermal degradation can occur at the high temperatures required to achieve the melt state. We have designed a series of polyurethanes that yield melts at low temperatures. This paper will discuss the effect of changing block length, keeping the other two key variables, composition and block incompatibility, the same.

Dynamic Mechanical experiments show that modulus vs reduced frequency mastercurves can be constructed at high temperatures for all materials. An increase in block length causes a failure of the time temperature superposition at low temperatures. Morphological investigations by Small-Angle X-Ray Scattering show that failure of superposition is related to a gradual increase in microphase separation as temperature is decreased. Similar observations have been made in diblock and triblock copolymers.

We also find that the mastercurves constructed by superposing data at high temperatures show reasonable agreement with the Rouse theory and the shift factors required for superposition agree well with the WLF equation. The primary effect of increasing block length is to increase the viscosity and longest relaxation time of the polymer; both these quantities show a power law dependence on molecular weight with surprisingly large exponents of about 5. This result can be obtained only with multiblock copolymers since the overall number of blocks is large enough to have minimal effect on viscoelastic properties; in diblock and triblock copolymers, an increase in block length necessarily causes an increase in overall molecular weight and the two effects cannot be separated.

Tuesday 11:25 San Carlos III GN18

VISCOELASTIC BEHAVIOR OF CUBIC PHASES IN BLOCK COPOLYMER MELTS

Mary Beth Kossuth, David C. Morse, and Frank S. Bates
Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

In recent years, much effort has gone into studying the rheological behavior of ordered block copolymers, mainly focusing on the classical phases of lamellae and hexagonally packed cylinders. The behavior of these two low symmetry phases is now fairly well understood. However, little work to date has been published on the rheological behavior of high symmetry phases such as spheres on a body-centered cubic lattice or the bicontinuous gyroid. The availability of nine chemically distinct block copolymer systems which form cubic microstructures has created the opportunity to examine the viscoelastic behavior of these high symmetry phases in detail. In particular, features of the frequency response of diblock copolymers are discussed in relation to entanglements and defects. The presence of at least one entangled block extends the limit of linear viscoelasticity. Defects are shown to suppress the characteristic plateau in the storage modulus. For a perfect single crystal, the rheological response is expected to be solid-like as w approaches 0. A universal viscoelastic pattern for cubic block copolymers is proposed which includes diblock and triblock sphere- and gyroid-forming materials of all molecular weights. The plateau modulus $G_{cubic}°$ is a result of linear viscoelasticity, while the low frequency crossover of $G'(w)$ and $G''(w)$, w_{xx}, is a nonlinear effect. A scaling law is developed which relates a physical characteristic of the microstructure to the mechanical behavior - namely, the characteristic domain spacing d^* to $G_{cubic}°$. A comparison of the experimental and theoretical scaling laws shows that experimental results lead to a scaling law of $G_{cubic}°/RT \sim d^{*3}$, while theory predicts $G_{cubic}°/RT \sim d^{*2}$.

Symposium EE
Extensional and Elongational Flow

Organizers: David James and Gareth McKinley

Tuesday 9:45 San Carlos II EE14

EXTENSIONAL VISCOSITIES OF POLYMER MELTS USING RME AND MÜNSTEDT RHEOMETERS: A COMPARATIVE STUDY

Jens Hepperle[1], Helmut Münstedt[1], Takushi Saito[2], Jonathan S. Schulze[2], Timothy P. Lodge[2], and Christopher W. Macosko[2]
[1]Institut für Werkstoffwissenschaften, Universität Erlangen-Nürnberg, Erlangen D-91058, Germany; [2]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

In an effort to compare the performance of available extensional rheometers, extensional viscosities of linear low density polyethylene (LLDPE) and polystyrene (PS) have been measured using the RME[1] (Rheometrics Scientific) and the Münstedt[2] oil bath rheometers. The RME rheometer benefits from the use of small samples, easy sample preparation, attainable Hencky strains of 6, and a maximum operating temperature of 350°C. However, the RME suffers from some disadvantages. Time delays in the RME instrument, probably caused by backlash in the gears of the belt motor, may produce lower measured viscosity values at short times and small deformations. Subtracting approximately 0.1 s from the time scale brings the RME data into better agreement with the Münstedt data. Artificial strain hardening effects observed at long times and large deformations may result from an inability of the measured force to return to its original zero force value at the end of the experiment. For example, the RME indicated a significant strain hardening of the LLDPE, especially at a strain rate of 1 s^{-1}; the Münstedt rheometer showed the LLDPE to be a non-strain hardening material. Both rheometers indicated the PS to be slightly strain hardening, and in general showed relatively good agreement.

1. Meissner, J. and J. Hostettler, Rheol. Acta 33, 1-21 (1994).
2. Münstedt, H., J. Rheol. 23, 421-436 (1979).

Tuesday 10:10 San Carlos II EE15

EXTENSIONAL VISCOSITY MEASUREMENTS ON SLIGHTLY BRANCHED POLYETHYLENES

Sujan Bin Wadud and Donald G. Baird
Chemical Engineering, Virginia Tech, Blacksburg, VA 25061-0211

Extensional viscosity measurements on linear polyethylenes(PE's) and slightly branched (i.e. a few long chain branches per chain) PE's are difficult to make because they tend to neck during extension. We investigate the stability of the extensional flow behavior of several PE's with varying molecular architectures. It is observed that although it is not possible to always generate uniform extensional flow, the stability of PE with a few long chain branches is noticeably different from that of a sample without branches. A novel method is used to force the PE's to deform homogeneously by encapsulating the sample of interest in a strain-hardening PE. From the rheology of the

strain-hardening sample and the composite sample, one can determine the extensional behavior of the slightly branched sample. The method appears to be promising, especially when samples of similar zero shear viscosities are used.

Tuesday 10:35 San Carlos II EE16

EXTENSIONAL RHEOLOGY AND FAILURE OF AN ABS POLYMER MELT

Chris E. Scott[1], Stanislav E. Solovyov[1], and Terry L. Virkler[2]
[1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; [2]Polymers Division, Bayer Corporation, Springfield, MA

The extensional viscosity and modes of failure are studied in start-up of steady uniaxial elongation for a thermoforming grade acrylonitrile-butadiene-styrene (ABS) polymer melt. The data are fit to one differential (PTT) and two K-BKZ type integral nonlinear viscoelastic constitutive models. Comparison of fit quality is performed and the PTT model is found to result in the best overall quality of fit. Experimental data for stress relaxation after both steady shear and uniaxial elongation are compared with the model predictions in order to evaluate their anticipated accuracy in prediction of residual stresses. Sample failure in terms of either the onset of non-uniform deformation during extension or the onset of non-uniform stress relaxation after extension is characterized. The observed failure points are compared to models which are available in the literature.

Tuesday 11:00 San Carlos II EE17

TRANSIENT VISCOSITY AND MOLECULAR ORDER IN A THERMOTROPIC POLYESTER LCP IN UNIAXIAL ELONGATIONAL FLOW

William A. Kernick and Norman J. Wagner
Chemical Engineering, University of Delaware, Newark, DE 19716

Thermotropic Liquid Crystalline Polymers (LCPs) are candidates for use as high strength materials, and such use typically involves polymer processing operations with some elongational character (such as fiber spinning, blow molding , or converging flow). It is of practical importance to understand the coupling between the rheology and the molecular orientation in LCPs. Towards this means, we present the transient viscosity and molecular orientation for a thermotropic polyester LCP under unaxial elongational flow.

Transient elongational measurements were obtained using a Rheometrics RME under inert atmosphere at 240 C. Complimentary shear measurements were performed under the same test conditions on an Rheometrics RMS800 controlled strain device. Under uniaxial elongation, substantial strain hardening is observed over two decades of strain rate, with the viscosity scaling with applied strain for strains greater than 1 Hencky strain. Additionally, Wide Angle X-ray Scattering (WAXS) measurements on quenched samples after elongation reveal a saturation in the molecular order parameter, independent of strain rate. The measured order parameters exceed the values measured previously under high shear, indicating the strong coupling of elongational flows to the molecular order.

The rheological results for steady shear flow are used to predict the elongational viscosity for the TLCP using the Doi theory for concentrated rod-like polymers. By comparison, it is concluded that the observed strain-hardening is the result of some new physics, and not the consequence of ideal LCP behavior. These results are important for understanding potential problems as well as advantages, i.e. flash reduction, of processing LCPs.

Tuesday 11:25 San Carlos II EE18

SQUEEZING FLOW WITH PARTIAL SLIP AT THE WALLS

Prashant V. Patil and Lynden A. Archer
Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122

In the limit of perfect slip at the walls, squeezing flow of polymer fluids between rigid parallel plates has long been known to create an equibiaxial elongation deformation field. Biaxial deformations are important in several commercial polymer processing flows, including plastics film blowing and blow molding. Liquid lubricants can in principle promote slip and thereby eliminate shear stress at the plates. In practice, however, these lubricants are themselves expelled from the plate region at high elongation rates and large strains, creating uncertainty about the

lubrication they provide. Liquid lubricants also tend to absorb slowly into the polymer under study creating even greater uncertainty about what material properties are actually deduced from lubricated squeezing flow measurements. In the present study we investigate squeezing flow of several linear and branched polybutadienes between rigid self-lubricating plates. As perfect slip is not necessarily guaranteed in this case, we analyze the problem as one of squeezing flow with partial slip at the walls. A comparison of the theoretical predictions for a generalized viscoelastic fluid with experimental data suggests that surfaces with bound fluorocarbon molecules provide sufficient lubrication that the shear stress contribution is negligible at most strain rates and strains considered. These results are confirmed by oblique angle flow-birefringence measurements that permit both stress components to be determined simultaneously.

Symposium IR
Interfacial Rheology and Rheological Modifiers

Organizers: Shi-Qing Wang, Stuart Kurtz and Bob Mendelson

Tuesday 9:45 Los Angeles IR5

DEVELOPMENT OF SHARKSKIN MELT FRACTURE AT THE DIE EXIT IN POLYBUTADIENE EXTRUSION

Yong Woo Inn[1], Robert J. Fisher[2], and Montgomery T. Shaw[1]

[1]Institute of Material Science, Polymer Program, University of Connecticut, Storrs, CT 06269-3136; [2]Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269-3222

We studied sharkskin melt fracture phenomena of polybutadiene (PBD), which exhibits similar flow properties and instabilities to linear low density polyethylene (LLDPE). The advantages of using PBD are that it exhibits larger distortions and slower development due to its high viscosity. By using a video camera with close-up lenses focused at the die exit, we observed the development of sharkskin in profile. It was shown that the sharkskin melt fracture develops with a cohesive failure at the die exit due to a peeling of surface layers as described by Howell and Benbow (1962). Oddly enough, this mechanism is similar to that proposed recently by Ovaici et al. (1998) for the extrusion of chocolate. A soap solution coating around the die exit to induce a slippery interface eliminated the sharkskin fracture, similar in the effect of fluoro-elastomer coating with LLDPE. Based on our visual observations, we qualitatively modeled the sharkskin fracture by combining Cogswell's (1977) idea on exit stretching at the die exit and the force balance of Ovaici et al. on the ring formation of the chocolate extrusion.

Tuesday 10:10 Los Angeles IR6

FLOW BIREFRINGENCE STUDY OF CAPILLARY EXTRUSION OF POLYBUTADIENE MELTS

Justin R. Barone and Shi-Qing Wang

Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

We have developed a capability to measure flow birefringence from slit-die flow of polymer melts in our lab. A number of applications of this method will be discussed, including investigation of stress growth and relaxation involving high stresses and interfacial rheological instabilities. Spatial and time-resolved flow birefringence measurements are carried out to examine the dynamics along the die of capillary flow of polybutadiene melts. It is found in a certain range of flow rate where "sharkskin-like" distortion occurs on the extrudate that flow birefringence oscillates periodically in the die exit region but remains constant in the die inland. The periodicity of the flow birefringence oscillation is found to be the same as that exhibited by the ripple-like sharkskin pattern, i.e., the time scale governing the time interval between two neighboring ripples. This study strongly supports the previously proposed interfacial molecular instability mechanism relating "sharkskin" to a periodic oscillation of the stress level within the die at the exit due to a fluctuating boundary condition between non-slip and slip [1]. The flow birefringence data on the sharkskin dynamics make the notion of rupture of the exiting melt at the contact line a rather unlikely origin of sharkskin formation.

[1] J.R. Barone, N. Plucktaveesak and S.Q. Wang, "Interfacial Molecular Instability Mechanism for Sharkskin Phenomenon in Capillary Extrusion of Linear Polyethylenes", J. Rheol., 42, issue 4 (1998).

Tuesday 10:35 Los Angeles IR7

RHEOLOGICAL MODIFICATION OF HDPE BY ADDITION OF VERY LOW CONCENTRATIONS OF TLCP

Chi Kwong Chan, Claire Whitehouse, and Ping Gao

Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

A high molecular mass polyethylene (HMMPE), with a wt avg MW of 350 000, cannot be processed beyond an apparent shear rate of approximately 30 s^{-1} at temperatures of 190, 230 and 250°C. After this there is pressure oscillation and melt fracture. The melt viscosity of this HMMPE ranges from 40 000 Pa s to 7000 Pa s and melt fracture starts at a wall shear stress of 210 kPa. When a novel thermotropic liquid crystalline polymer (TLCP) based on hydroxybenzoic acid, hydroquinone and sebacic acid is added to the HMMPE at concentrations of 0.5, 1 and 2 wt%, viscosity reductions 90% are observed at 190°C and 230°C. The onset of melt fracture is delayed to wall shear stress values of up to 417 kPa and the processing window for this HMMPE has been expanded up to 300 kPa and 900 s^{-1}.

The TLCP has a crystalline-nematic transition at 169°C and a nematic-isotropic transition from 185°C to 262°C. At 190°C and 230°C it is a biphase, but mainly nematic at the lower temperature and mainly isotropic at the higher with a viscosity always <10 Pa s. The flow curves generated by capillary and rotational rheometry indicate different viscosity reducing mechanisms taking place consecutively and concurrently, dependent on the phase condition of the TLCP and the TLCP:PE viscosity ratio. These mechanisms include the deformation and elongation of the TLCP droplets under shear and the alignment of the nematic phase within the TLCP regions which causes the forced alignment of the neighbouring HMMPE molecules. It is postulated that there is a boundary of PE alignment that increases through the matrix, making the viscosity reduction a bulk phenomenon. This is confirmed by wall slip measurements. At the higher temperature there is also a phase transition from isotropic to nematic: producing a larger quantitiy of nematic phase which contributes to the viscosity reduction.

Project funded by grant no. HKUST 664/96P.

Tuesday 11:00 Los Angeles IR8

EXTRUSION OF POLYOLEPHINS AND FLUOROPOLYMERS WITH A NEW PROCESSING AID

Eugene E. Rosenbaum[1], Stuart K. Randa[2], Savvas G. Hatzikiriakos[1], and Charles W. Stewart[2]

[1]Department of Chemical Engineering, The University of British Columbia, Vancouver, BC V6T 1Z4, Canada; [2]DuPont Fluoroproducts, DuPont De Nemours & Co, Wilmington, DE

The influence of a new processing aid (a composition of fine particles of boron nitride) on the rheology and processing behavior of polyolefins and fluoropolymers in extrusion is studied. The equipment used includes both an Instron capillary rheometer with two types of dies, namely capillary dies and special annular dies (Nokia Maillefer wire coating crosshead) attached to the rheometer, and an extruder. A metallocene polyethylene and several TeflonÒ fluoropolymers were tested using these two pieces of equipment. The additive had no or very little effect on the extrudate appearance in the capillary geometry (both capillary and orifice dies with a different entrance angle were tested). The greatest influence of the additive occurs in crosshead dies and tips with a streamlined flow, where the additive particles seem to enhance melt slippage and relieve internal stresses. This action eliminates surface melt fracture and postpones the critical shear rate for the onset of gross melt fracture to significantly higher values depending on resin type, temperature, and the additive content. To explain a possible mechanism of the effect of the additive on the processability of the resins, rheological measurements by means of both a parallel-plate and sliding-plate rheometers were carried out. The rheology of the resins did not seem to change much with an addition of boron nitride except for the low-shear-rate (low-frequency) range where the behavior of the filled resin was found to be similar to that of a crosslinked polymer. The practical wire coating and tubing extrusion studies with these resins were also carried out.

Tuesday 11:25 Los Angeles IR9

BLOCK COPOLYMERS AS RHEOLOGY MODIFIERS FOR POLYPROPYLENE

Todd D. Jones, Frank S. Bates, and Christopher W. Macosko
Department of Chemical Engineering and Materials Science, University of Minnesota,
Minneapolis, MN 55455

Block copolymers exhibit interesting rheological properties, due to their unique molecular architectures. These architectures also provide opportunities for modifying properties of homopolymers through blending. We have recently prepared blends containing small amounts (~2%) of polystyrene-hydrogenated polybutadiene block copolymers of various microstructures in polypropylene by mixing in a Haake melt mixer. Typically, these additions increased the zero shear rate viscosity, relative to the unmodified homopolymer. However, decreases of as much as 30% in the zero shear rate viscosity were also observed. Transmission electron microscopy of these blends showed a variety of morphologies, including dispersed micelles, aggregated micelles, and vesicles. These morphologies correlate with the observed changes in viscosity. The different morphologies are proposed to form due to variations in the block copolymer microstructure. Studies of variation in block copolymer architecture and polymer molecular weight will provide further insight into this correlation between morphology and rheology.

Tuesday Afternoon

Symposium VP
Viscoelastic Processing Flows: Theory and Experiment

Organizers: Albert Co and Bamin Khomami

Tuesday 1:30 San Carlos I VP6

NUMERICAL SIMULATIONS OF FREE SURFACE VISCOELASTIC FLOWS USING LEVEL-SET METHOD

Felix Alcocer[1], Pushpendra Singh[1], and Gary Leal[2]
[1]Mechanical Engineering, NJIT, Newark, NJ 07102; [2]Chemical Engineering, University of California - Santa Barbara, Santa Barbara, CA 93106

A code based on the level-set method is developed for simulating the free surface flows of viscoelastic fluids modeled via the FENE dumbbell and Oldroyd-B models. The code is used for simulating the motion of the viscoelastic drops in Newtonian fluid, as well as the motion of the Newtonian drops in viscoelastic fluids. The method is also used for simulating the time dependent filling patterns in the two dimensional molds. The viscoelastic algorithm is based on a splitting method that decouples the problems associated with the convection and viscoelasticity. The resulting sub-problems are discretized using the finite element method and solved using a preconditioned generalized minimum residual method.

Tuesday 1:55 San Carlos I VP7

THE FLOW OF POLYMER MELTS THROUGH A MODEL POROUS MEDIUM

William H. Hartt[1] and Donald G. Baird[2]
[1]Miami Valley Laboratories, Procter and Gamble Company, Cincinnati, OH 45253-8707;
[2]Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24060-0211

This paper is concerned with the numerical simulation of the flow of two polymer melts of significantly different rheological properties through an idealized porous medium consisting of cylinders arranged in a square packing configuration and the comparison of predictions of pressure drops with experimental values. It was found for LDPE, which is highly strain-hardening with a relatively broad spectrum of relaxation times, that computations with a purely viscous model (GNF model with a Bird-Carreau empiricism for viscosity) under-estimated the pressure drop by about 100%. Computations with the PTT model, which more accurately represented the extensional and transient response of LDPE, agreed well with the pressure drop data up to the loss of convergence. For LLDPE, which is strain softening and has a narrower distribution of relaxation times, computations with the GNF model over-predicted the pressure drops while those using the PTT model were in good agreement with the data. By studying the predictions of stress along the centerline between two cylinders, one could identify the role of the constitutive equation in fitting the extensional and transient flow behavior on the predictions of pressure drop.

Tuesday 2:20 San Carlos I VP8

MULTILAYER FILM CASTING OF POLYETHYLENE MELTS: MODELING AND EXPERIMENTS

Baigui Bian and Albert Co

Department of Chemical Engineering, University of Maine, Orono, ME 04469-5737

The multilayer film casting involving a LDPE melt and a LLDPE melt was investigated. Parameters of a Giesekus model were estimated for these melts. These were chosen to follow observed extensional behavior. Numerical simulations were conducted using the estimated model parameters. The calculated results were compared with experimental velocity profiles and film tension measured at various draw ratios and thickness fractions of the two polymer melts.

Tuesday 2:45 San Carlos I VP9

IMPACT OF VISCOELASTICITY ON GAGE VARIATIONS IN FILM CASTING

Dilip Rajagopalan

Central Research and Development, E. I. Dupont and Company, Wilmington, DE 19880

Mathematical modeling of the melt draw step in film casting is used to understand the impact of viscoelasticity on gage variations. The thin film approximation is used to simplify the governing equations to a set of two-dimensional partial differential equations which are solved using the finite element method. Gage variations caused by a periodic variation in die lip opening are studied using the Giesekus constitutive equation. The magnitude of gage variations increases with increasing Deborah number and increasing melt draw ratio. The mechanism of this gage magnification is related to the extension thickening rheology predicted by the Giesekus model.

Tuesday 3:35 San Carlos I VP10

VISCOUS HEATING AND NON-ISOTHERMAL HYDRODYNAMICS IN POLYMER SOLUTIONS

Mark T. Arigo[1], Leif E. Becker[1], and Gareth H. McKinley[2]

[1]Division of Engineering and Applied Science, Harvard University, Cambridge, MA 02138;
[2]Dept. of Mechanical Engineering, M.I.T., Cambridge, MA 02139

Ideal elastic fluids provide model systems for probing the importance of non-isothermal rheological phenomena such as viscous heating in polymer processing flows. In the present work we present quantitative measurements of such effects in shearing flows of viscous polymeric solutions. The test fluids consist of a Newtonian oil (oligomeric polystyrene) and an ideal elastic fluid consisting of 500ppm high molecular weight monodisperse polystyrene dissolved in the polystyrene solvent. Using standard cone-and-plate and parallel plate rheometers, the effects of viscous heating on the viscometric properties are explored. Viscous heating effects are characterized by a Nahme-Griffith number, $Na = b h_0 U^2 / k T_0$. In shear flows with $Na \sim O(1)$, viscous heating effects become significant and lead to noticeable deviations in the fluid rheology. Under controlled-rate conditions, the stress/shear-rate curve becomes double-valued at large Na, as predicted theoretically, and both states are hydrodynamically stable and can be attained experimentally. However, under controlled stress conditions, the shear flow becomes unstable when a critical maximum stress is exceeded and the fluid undergoes `thermal blow-up.' Two-dimensional simulations provide quantitative comparison to both the steady and transient experiments when the thermal boundary conditions at fluid/solid interfaces are accurately characterized. The spatial temperature distribution in the flow can be quantified *in situ* using thermochromic liquid crystal sheets placed on the boundary. For torsional shear flows, a radial distribution of temperature is found with the maximum temperature near the outer edge and the coolest spot at the center. Similar viscous heating effects can also be generated in pressure-driven flows through a thin slit, and we discuss the resulting thermal entrance-region flow and the effects of viscous heating on die-swell and extrudate stability.

Tuesday 4:00 San Carlos I VP11

FLOW ANALYSIS AND EXPERIMENTAL VERIFICATION OF GAS-ASSISTED INJECTION MOULDING

Rui-Feng Liang, Dong-Yan Wang, Xiao-Zhong Qu, and Rong Chen
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Gas-assisted injection molding (GAIM) is an innovative technology which has attracted significant recent interest. Most GAIM process involves a competition between a polymer melt flow front and a pressurised gas penetration front within the moulding and requires a precise control of pressure and time of injected gas and in general gives rise to more difficulties in mould and process design than conventional injection molding. Computer aided flow analysis provides an effective way to overcome this problem and has proved to be very important in achieving the successful application of GAIM. This paper reports our work on two test moulds and two production moulds using gas-assisted injection molding. Flow analyses were carried out, either to optimize mould structural design and process design or to simulate typical experimented processes, by using C-Mold software (AC Technology, USA) incorporated with test material parameters for modified Cross viscosity model. Experiments were conducted with four moulds individually by using GAIM equipment (Gas Injection Ltd, UK) combined with different injection moulding machines. Effects of melt injection positions and process parameters, gas injection positions and process parameters, gas channel distributions, and rheological properties of polymer melts have been discussed. Numerical simulation results have been compared to the experimental results wherever possible. In terms of the matching between simulation and experiment, the reliability of C-Mold predictions for one test mould has been evaluated. Fingering effect has been discussed for the other test mould which consists of walls with different thickness. Some guidelines are discussed for the two production moulds. It has been demonstrated that GAIM process presents plenty of advantages and benefits over a conventional injection molding.

Tuesday 4:25 San Carlos I VP12

EVALUATION OF CONSTITUTIVE EQUATIONS FOR PVC FORMULATIONS IN EXTRUSION DIES

Terje Glomsaker[1], Einar L. Hinrichsen[2], Fridtjov Irgens[1], Age G. Larsen[2], and Pål Thorsteinsen[3]
[1]Div. of Appl. Mechanics, Norwegian University of Science and Technology, Trondheim N-7034, Norway; [2]Dept. of Polymers and Composites, SINTEF Materials Technology, Oslo N-0314, Norway; [3]Technical Centre PVC, Hydro Polymers Nordic, Porsgrunn N-3910, Norway

Un-plastisized PVC have a peculiar melt rheological behaviour compared to most thermoplastic polymers. The reason is that PVC is normally processed at temperatures where the crystalline and mesomorphic regions are only partially melted. We investigated different methods for measuring rheological properties of PVC formulations, relevant for modelling of extrusion. In order to investigate self-consistency of numerical models, we fitted model parameters for non-isothermal inelastic and non-linear viscoelastic constitutive equations to the measured material functions, and performed numerical simulations of extrusion experiments.

The shear viscosity was measured at different temperatures in capillary rheometers and in-line after an extruder. The Mooney technique was utilized for estimating slip velocities. Elongation properties have been estimated from entrance flow, and the linear dynamic moduli were measured in a parallel plate rheometer. The thermo-mechanical history of the test material was found to influence the elastic and elongational properties, as well as other material functions, at a given temperature. For some formulations, the flow curves obtained from the capillary rheometers were disturbed by an 'instability' that is not fully understood. The effect was more pronounced for low temperatures and long dies. Although slip could not be proven or separated from temperature effects in any of the capillary experiments, boundary conditions are important in order to understand this effect.

The non-isothermal inelastic simulations of the capillary flow showed in some cases in-consistency with the experimental data at high shear rates, indicating a combination of slip and temperature effects. Both the K-BKZ equation with an exponential damping function and the PTT model fit the linear dynamic moduli and the shear viscosity in a large range of shear rates. However, the Bagley correction was underestimated compared with that predicted from simulations for both inelastic and viscoelastic equations.

Tuesday 4:50 San Carlos I VP13

PERFORMANCE OF THE GENERALIZED NEWTONIAN FLUID MODEL IN A COMPLEX FLOW OF VISCOPLASTIC MATERIALS

Luiz M. Freire, Paulo R. Souza Mendes, Mônica F. Naccache, and Luiz F. Azevedo
Department of Mechanical Engineering, Pontifícia Universidade Católica, Rio de Janeiro, RJ 22453-900, Brazil

Flows of viscoplastic liquids through abrupt axisymmetric expansions are present in a number of manufacturing and packaging industrial processes. Numerical simulations of this type of flow are typically obtained with the aid of the Generalized Newtonian Fluid (GNF) model together with a viscosity function that involves an yield stress.

The Bingham viscosity function cannot be used in complex flows, because it does not allow deformation at stress levels below the yield limit. To handle this and the singularity of Bingham's viscosity function, an approximation has to be done. Some alternative viscosity functions have been proposed, such as the bi-viscosity and the Papanastasiou ones. However, experimental evidence that these models predict accurately the velocity and stress fields is rather scarce and inconclusive.

In this work, an experimental study is done in order to investigate the prediction capability of these alternative viscosity models. A flow visualization of a viscoplastic material through an abrupt axisymmetric expansion is performed, using a PIV technique. Also, numerical solutions are obtained using a finite volume method to solve the governing conservation equations, using the GNF with the bi-viscosity model. The measured pressure drops and velocity fields are compared to those obtained numerically.

Symposium CF
Coupling Flow and Order in Fluids

Organizer: Lynn Walker

Tuesday 1:30 San Carlos III CF1

SHEAR INDUCED TWIST AND SPLAY IN NEMATIC LIQUID CRYSTALS

David M. Boudreau[1], C. Peter Lillya[1], Richard Stein[1], and H. Henning Winter[2]
[1]Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003;
[2]Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts

The effect of shear upon the molecular orientation of flow aligning liquid crystals (MBBA and 5CB) was investigated by preparing monodomains with director alignment within the shear plane (planar alignment, $\theta=0^o$), but with varying initial alignment between the shear direction ($\phi_0=0^o$) and the vorticity direction ($\phi_0=90^o$). Conoscopy was used to measure both the twist (ϕ) and splay (θ) rotations of the director. In shear experiments with monodomains which are initially aligned in the direction of shear, the director rotates 30% faster than predicted by the Leslie-Ericksen model. By increasing the initial alignment angle (ϕ_0), angular rotation for both director twist and splay are slowed down (retardation period at onset of shear). The measured steady state alignment angle (represented by the Leslie angle) increases slightly with increasing ϕ_0 Different time functions govern the relaxation of director splay and twist. While splay relaxation occurs rapidly and is independent of ϕ_0, twist relaxation is slow and increases with ϕ_0. Experiments with polymeric systems are in progress.

Tuesday 1:55 San Carlos III CF2

DYNAMICS AND ALIGNMENT BEHAVIOR OF A THERMOTROPIC LIQUID CRYSTALLINE POLYMER

Weijun Zhou[1], Julia A. Kornfield[1], Victor M. Ugaz[2], and Wesley R. Burghardt[2]
[1]Chemical Engineering, Caltech, Pasadena, CA 91125; [2]Department of Chemical Engineering, Northwestern University, Evanston, IL 60208

Mechanical rheometry and *in situ* flow-WAXS techniques are used to characterize the flow behavior of a model thermotropic liquid crystalline polymer (DHMS-7,9). We observed two modes of molecular alignment under steady shear flow. Depending on the temperature and applied shear rate, the molecules can be aligned along either the flow direction ("parallel" alignment) or the vorticity direction ("perpendicular" alignment). We have studied the effect of orientation on linear viscoelasticity behavior. Above a crtical frequency, ω_c, the dynamic moduli are insensitive to the state of alignment. Below ω_c a siginificant drop in the dynamic modulus was observed for oriented samples. This drop in modulus is much larger for samples with parallel orientation than perpendicular orientation. Upon flow inception, the transient response of the first normal stress difference (N_1) was qualitatively different for these two alignment processes. For perpendicular alignment a large negative undershoot of N_1 was followed by a gradual recovery to the steady state. In contrast, for parallel alignment, N_1 was found to be always positive. Molecular orientations could be flipped from parallel to perpendicular, and vice versa, by applying a step change of shear rate. A tentative mechanism for this flow-alignment behavior will be discussed on the basis of the rheological and WAXS observations.

Tuesday 2:20 San Carlos III CF3

EFFECT OF SPACER LENGTH ON THE RESPONSE OF MICROSTRUCTURE TO FLOW IN THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

Patrick T. Mather[1], Hong G. Jeon[2], C. D. Han[3], and S. Chang[3]
[1]Materials Directorate, Air Force Research Lab, Wright Patterson AFB, OH 45433-7750; [2]Systran Corp., Air Force Research Lab, Wright Patterson AFB, OH 45433-7750; [3]Polymer Engineering, University of Akron, Akron, OH 44325

The evolution of disclination-based microstructure within steady shear flow plays an important role determining the macroscopic rheological properties of liquid crystalline polymers (LCPs). It is hypothesized that the stiffness of LCP chains should influence the microstructural evolution through its influence on the intermolecular potential and the complex coupling of order and flow. While this concept is generally accepted, no study using in-situ microstructural probes on a system with systematically altered chain stiffness has been pursued. We present the results of such a study, in which we use several novel rheo-optical methods on a series of main-chain thermotropic polymers (PSHQn) in which n is varied from 3 to 12. Such phenomena as the isotropic-nematic transition, shear stress overshoot during start-up, shear flow-alignment, and band formation will be discussed. Rheo-optical techniques utilized include polarizing optical microscopy, small-angle light scattering, and birefringence measurements. Particular focus is aimed at the influence of the chain stiffness on these rheological phenomena.

Tuesday 2:45 San Carlos III CF4

EFFECT OF SHEAR INDUCED PHASE TRANSITIONS ON THE RHEOLOGY OF A THERMOTROPIC COPOLYESTER HBA/HQ/SA

Ping Gao and Huanli Lei
Chemical Engineering, Hong Kong University of Science and Technology, Hong Kong, Hong Kong

Rheo-optical experimental measurements were performed on a thermotropic copolyester HBA/HQ/SA using a combination of an optical shearing apparatus and a dynamic mechanical spectrometer, Rheometrics RMS 800. The measurements were performed at three different temperatures, 170 °C, 190 °C and 230 °C, respectively. At these temperatures the material exhibits predominantly smectic C, nematic and isotropic phases respectively.

The dynamic frequency sweep data show that the loss moduli dominate the storage moduli at all frequencies tested at 190 °C. At 170 and 230 °C, the loss moduli dominate the storage moduli at low and high frequencies,

respectively. Steady shear measurements were also performed at 190 °C and 230 °C, respectively. It is observed that the material follows Cox-Merz rule at 190 °C. At 230 °C, the complex viscosity dominates the steady shear viscosity initially and at high frequencies, the two become congruent.

These rheological results are linked with the melt structure evolution during shear. It is observed that the isotropic phase starts to show phase transitions into mesophases at a certain critical shear rate and the amount of mesophase increases with increasing shear rates. At a shear rate of, say, 30 1/s, the material appears to show a full transition within the optical resolution limit. Phase transitions are also observed at 170 °C during shear. At small shear rates the initially fan shaped smectic C texture was observed to break up during shear followed by the appearance of loop defect textures characterizing nematics. At high shear rates the material again becomes more ordered and displays smectic C texture with point defects.

Tuesday 3:35 San Carlos III CF5

EVIDENCE OF LIQUID CRYSTALLINE RHEOLOGY IN POLYETHYLENE MELTS

Ibnelwaleed A. Hussein and Michael C. Williams
Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada

High-density polyethylene (HDPE) melts have previously been identified as having an unusually high degree of molecular order, but the rheological implications of this have heretofore not been explored. This has been a serious oversight, inasmuch as HDPE melt processing is one of the major tasks of the world's polymer industry. Here, we investigate several industrial samples of HDPE, covering the range of molecular weight (8.5-13.7x 10^{4}) and temperature (190^{o}&ltT<250^{o}C) using a Rheometrics Mechanical Spectrometer 800. Remarkable manifestations of liquid-state order are found that agree with theoretical predictions for a liquid-crystal polymer (LCP). These include indications of an approach to a sign change in $N_1(\gamma)$ at low values of the steady shear rate, γ, and a kink in the Non-Newtonian viscosity $\eta(\gamma)$. Some evidence on transient normal and shear stress and on dynamic properties $G'(\omega)$ is also presented. The collective data appear to confirm that the HDPE melt may be considered to be a LCP, and also that the LCP rheological theories can be applied.

Tuesday 4:00 San Carlos III CF6

X-RAY SCATTERING MEASUREMENTS OF MOLECULAR ORIENTATION IN CHANNEL FLOWS OF A THERMOTROPIC LIQUID CRYSTALLINE POLYMER

David K. Cinader, Jr. and Wesley R. Burghardt
Department of Chemical Engineering, Northwestern University, Evanston, IL 60208

We have constructed a channel flow extrusion die which allows collection of x-ray scattering patterns as a function of position in the die. A single-screw extruder is used to pump the melt while interchangeable spacers allow the channel flow geometry to be altered. Available geometries include contractions and expansions of sharp and gradual character, as well as a simple slit flow. We present studies of a commercial liquid crystalline polymer (Xydar resin supplied by Amoco). In slit-contraction flows, orientation increases modestly in the expansion region, followed by a gradual decrease in the straight downstream channel. Conversely, slit-expansion flows lead to a substantial decrease in orientation followed by a recovery in the straight downstream channel. Scattering patterns reveal orientation transverse to the flow direction induced by unfavorable extensional gradients. This mixed orientation state manifests itself as a four spot scattering pattern reflecting the coexistence of downstream and transverse orientation in the expansion region. Analysis of the two dimensional scattering patterns allows extraction of quantitative measurements of the average degree and direction of molecular orientation as a function of position within these flows.

Tuesday 4:25 San Carlos III CF7

EXTENSIONAL FLOW EFFECTS ON MORPHOLOGY DEVELOPMENT IN LIQUID CRYSTALLINE POLYMERS

John R. Dorgan and Dong Yan
Chemical Engineering Department, Colorado School of Mines, Golden, CO 80401-1887

In polymer processing one of the strongest influences on morphology is flow and deformation. The KevlarTM family of polymers made by DuPont is the best know example of liquid crystalline polymers and is primarily sold and used as high tenacity fibers; in fiber spinning a strong extensional flow field is imposed. In this work, the effects of an imposed extensional flow field on morphology development in liquid crystalline polymers is examined in the context of a time dependent Landau-Ginzburg model.

From a fundamental point of view, coupling flow effects to thermodynamic Hamiltonians is difficult and generally requires a potential flow. Extensional flow is a potential flow so the appropriate terms can be formulated and added to the free-energy. Here, a term representing the flow is added to the free energy of the Flory-Ronca lattice theory of the nematic state. In terms of the effects on the equilibrium phase diagram, the extensional flow helps to orient the LCP chains so that the nematic phase is formed at lower concentrations. In addition, for a given concentration the calculations show that the nematic phase is more ordered during flow than under quiescent conditions. Finally, the spinodal line for the nematic phase is suppressed to lower temperatures than in the absence of flow. The effects of flow on phase separated morphology are presented. These are easily understood in the context of a convected coordinate system which moves with the material. Results are presented in terms of the stationary frame of reference and show the deformation and elongation of the concentration field in the direction of flow.

Effects including concentration, molecular weight, quench depth beneath the spinodal, and solvation strength are discussed.

Tuesday 4:50 San Carlos III CF8

MANIPULATING LCP ORIENTATION IN CHANNEL FLOWS

Jimmy Feng[1], Giorgia Sgalari[2], and Gary Leal[2]
[1]The Levich Institute and Mechanical Engineering Department, The City College of New York, New York, New York 10031; [2]Department of Chemical Engineering, University of California - Santa Barbara, Santa Barbara, CA 93106

One difficulty in injection molding LCP materials is the proliferation of orientational defects called disclinations. It is generally believed that director tumbling plays a major role in generating such defects. In this work we use numerical simulations based upon the Doi theory to explore the possibility of controling LCP order and director dynamics in channel flows by manipulating the geometry of the channel and by using slip boundary conditions. The main ideas are that the entensional flow caused by a contraction in the channel and apparent slip by using lubricants at the walls may suppress director tumbling in the channel, and hence minimize the generation of defects in injection molding. Results show that a contraction effectively suppresses director tumbling in the central region of the channel. A slip boundary condition reduces shear near the wall and is also beneficial.

Symposium EE
Extensional and Elongational Flow

Organizers: David James and Gareth McKinley

Tuesday 1:30 San Carlos II EE19

CONTRACTION/EXPANSION FLOWS OF NON-NEWTONIAN MONOLAYERS

David J. Olson and Gerald G. Fuller
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

Langmuir monolayers, which consist of amphiphilic molecules at the air-water interface, can be represented as two-dimensional fluids. Such fluids may be Newtonian, or may exhibit highly nonlinear flow behavior. By inducing surface pressure-driven flow by means of a movable barrier, we performed entry flow and exit flow experiments on Langmuir monolayers of arachidyl alcohol; poly(para-phenylene sulfonic-acid) (PPPSH) solutions; and poly(octadecyl methacrylate) (PODMA). Streamlines were characterized by seeding the monolayer with sulfur particles and capturing images on videotape. Arachidyl alcohol, a Newtonian monolayer, exhibited no observable vortices in the upstream channel corner when forced through a 4:1 contraction. Furthermore, the addition of the rigid rod polymer PPPSH (25 mol%) to the arachidyl alcohol produces no vortices. In contrast, experiments on PODMA, a flexible chain polymer, reveal large vortices in the upstream channel corner. This is consistent with the idea that vortices act as stress-relief mechanisms for materials in which large extensional stresses can accumulate. The streamlines of the exit flow experiments on the three monolayers provide evidence of the presence of a non-zero normal stress difference in the monolayers.

Tuesday 1:55 San Carlos II EE20

ELONGATIONAL FLOW OF SOLUTIONS OF HYDROPHOBICALLY MODIFIED POLYMERS AND SURFACTANTS

Santipharp Panmai[1], Robert K. Prud'homme[1], and Dennis G. Peiffer[2]
[1]Department of Chemical Engineering, Princeton University, Princeton, NJ 08544; [2]Polymers & Fluids Laboratory, Exxon Research and Engineering Company, Annandale, NJ 08801

Elongational and shear viscosities of aqueous solutions of hydrophobically modified polymers (hm-polymers) with spherical and rod-like surfactant micelles have been measured. Hydrophobically modified hydroxyethylcellulose with 0.9% and 1.3%mole pendent C_{16} hydrophobes (C_{16}HEC) and unmodified HEC (M_W ~ 250,000) were studied. The surfactant used was cetyltrimethylammonium bromide (CTAB), which forms spherical micelles and, with equimolar sodium salicylate (NaSal), rod-like micelles. Solutions of randomly grafted hm-polymers with spherical micelles display shear-thinning and elongational-thickening behaviors. These rheological properties can be described and fitted with a model for associating telechelic polymers by Tanaka and Edwards (1992), which predicts elongational thickening from enhanced hydrophobe associations in elongational flow. In dilute solution of rod-like micelles, hydrophobic associations with hm-polymers hinder rod alignment and suppress micellar growth in both shear and elongational flows. In semidilute solution of rod-like micelles, chain alignment and extension in elongational flow are facilitated by associations with hm-polymers, which increase the apparent friction coefficient between micellar rods.

Tuesday 2:20 San Carlos II EE21

POROUS MEDIA FLOW OF POLY(ETHYLENE OXIDE)/SODIUM DODECYL SULFATE MIXTURES

Alejandro J. Muller[1], Celsa M. DaRocha[1], Nelson Ramirez[1], and A. E. Saez[2]
[1]Ciencia de los Materiales, Universidad Simon Bolivar, Caracas 1080-A, Venezuela; [2]Chemical Engineering, North Carolina State University, Raleigh, NC 27695

It is well known that solutions of high-molecular-weight, flexible polymers exhibit extension thickening effects when they flow through porous media where the flow exhibits strong elongational components. Typically, the extension thickening occurs after a specific value of the fluid Reynolds number (or the average strain rate) is reached, and the observed abrupt increase in the apparent viscosity might be of an order of magnitude or more. In this work, we explore the behavior of solutions of mixtures of poly(ethylene oxide) (PEO) and an anionic surfactant, sodium dodecyl sulfate (SDS) when they flow through disordered packings of glass spheres. The effects of changing the polymer and surfactant concentrations, as well as the ionic environment were studied. For a fixed polymer concentration, adding SDS at concentrations below the CAC (critical aggregation concentration) results in no effect on the apparent viscosity of the solution. However, at or above the CAC, an increase in surfactant concentration produces the following effects: the onset Reynolds number decreases, the maximum value of the apparent viscosity reached after extension thickening increases, and the criticality of the extension thickening effect increases. Adding NaCl to the system results in stronger extension thickening effects with lower onset Reynolds numbers, even at smaller SDS concentrations as compared to equivalent PEO/SDS solutions in deionized water. The results were rationalized in terms of the aggregation of SDS micelles along the polymer chain: the micellar aggregates affect the conformation of the chains and therefore their ability to form transient entanglement networks. The results obtained show that the extension thickening behavior of a polymer solution in an elongational flow situation can be manipulated by adding a surfactant that forms ionic aggregates along the polymer chain.

Tuesday 2:45 San Carlos II EE22

SOME DESIGN CRITERIA FOR THE CONVERGENT CHANNEL AS AN EXTENSIONAL RHEOMETER

Paulo R. Souza Mendes, Roney L. Thompson, and Angela O. Nieckele
Department of Mechanical Engineering, Pontifícia Universidade Católica, Rio de Janeiro, RJ 22453-900, Brazil

An important aspect while designing an "R^2z = Constant" convergent channel as an extensional rheometer is the appropriate choice of the geometrical parameters and of the Reynolds number range of operation. The higher is the Reynolds number value, the thinner will be the boundary layer where the undesirable no-slip effect is confined, as discussed in the literature. However, large values of the Reynolds number may cause undesirable effects, such as non-negligible viscous heating. Therefore, one design task is to find a range of Re within which the boundary layer is thin enough, and the velocity field in most of the domain is reasonably close to the desired kinematics. In this work we obtained numerical solutions for the flow of a Newtonian fluid through a convergent channel, for representative ranges of Re, dimensionless channel length, L, and dimensionless axial coordinate of inlet section, z_0. For all cases, we determined fields of flow type, where regions of shear and of extension can be visualized.

Symposium SL
Rheology of Solids

Organizers: Andre Lee and Gregory B. McKenna

Tuesday 3:35 San Carlos II SL1

ON THE FINITE ELASTICITY AND HYPO-ELASTICITY

Arkady I. Leonov
Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

Thermodynamic approaches to finite elasticity are almost generally accepted. Nevertheless, there still is a lack of proof for the necessity of potential strain-stress relations in generally defined elasticity and hypo-elasticity. This situation has resulted in ambiguous applications of the general concept of elasticity to the description of irreversible phenomena in viscoelastic solids and liquids. The report makes a brief review of the general concepts of elasticity and hypo-elasticity, with most attention paid to the Eulerian description, employed in viscoelastic theories. Then it is demonstrated that all hypothetical materials with non-potential finite elastic or hypo-elastic constitutive relations can create an energy from nothing, i.e. work as perpetual motion machines. This gives a "physical" proof of necessity of potential conditions in general finite elasticity and hypo-elasticity and their extensions to finite viscoelasticity.

Tuesday 4:00 San Carlos II SL2

INVESTIGATIONS OF NONLINEAR MATERIAL BEHAVIOR USING SIMULTANEOUS MEASUREMENTS OF VOLUME RECOVERY AND PHYSICAL AGING

Carl R. Schultheisz and Gregory B. McKenna
Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

In passing from above to below the glass transition, amorphous polymers evolve slowly toward thermodynamic equilibrium. This evolution can be observed in measurements of the volume, enthalpy, optical properties and mechanical properties of the material. Some experimenters have reported differences in the rate of equilibration or time required for equilibration of different properties, which implies that models of this behavior would need to be fairly complex, requiring different "clocks" to describe each property. Typically, such comparisons of different properties must be made using different samples in different instruments, leading to questions about the comparability of the materials or thermal histories. Using the NIST Torsional Dilatometer, measurements of volume recovery and mechanical response can be made simultaneously. Experiments using an epoxy have been performed using upward and downward temperature jumps, after which the sample is subjected to intermittent torsional deformations to follow the evolution of the mechanical properties; the torsional deformation also induces a volume change (comparable to the volume change caused by the temperature jump) and a normal force along the axis of the cylindrical sample. Several earlier experiments from this laboratory suggested a difference in time scales for equilibration of the volume recovery and the evolving viscoelastic response during aging. However, recent experiments seem to indicate that the volume and mechanical behavior (torque and normal force) equilibrate at the same time. The current data and analysis methods will be compared with the prior experiments and methods. In addition, it has been found that the torque, volume and normal force in each twist step have different relaxation behaviors. We also find that the epoxy has exhibited significant chemical aging, as manifested by increasing relaxation times, over the (3 year) course of the experiments.

Tuesday 4:25 San Carlos II SL3

TORSION OF A POLYMER ROD UNDERGOING MICROSTRUCTURAL CHANGES

Alan S. Wineman
Department of Mechanical Engineering and Applied Mechanics, University of Michigan, Ann Arbor, MI 48109

The torsion of solid circular rod of a polymeric solid is discussed when the material undergoes microstructural changes due scission and re-cross linking of network junctions. The constitutive equation for the polymer is based on the two network theory introduced by Tobolsky and later generalized by Fong and Zapas. It is assumed that there is no scission within a range of deformation from the initial state. Beyond this range, in each increment of deformation, some volume fraction of the material undergoes scission and can then re- cross link to form a new network with a new reference state. The constitutive equation can represent different responses on load and unload, permanent set on removal of load, and anisotropy of response on reloading. The consequences of this material response when there is spatially varying strains due to torsion is analyzed. The discussion shows the evolution of regions of original and modified material, the softening effects associated with the process of scission and re-cross linking and the occurrence of residual stress and deformation on removal of load.

Tuesday 4:50 San Carlos II SL4

A COMPLETE SECOND ORDER NONLINEAR VISCOELASTIC MODEL FOR AMORPHOUS POLYMERS

G. Medvedev, P. Shirkhande, and J. M. Caruthers
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

Nonlinear viscoelastic constitutive equations developed via Rational Mechanics or any alternative thermodynamic theory are determined from a nonequilibrium Helmholtz free energy, which must be represented at least through second order Frechet terms. This Helmholtz potential will generate both single and double integral contributions in the stress, entropy, enthalpy, etc. constitutive equation; however, the double integral contributions are typically neglected in comparing constitutive predictions with experimental data. In this communication we will examine the

predictions of these double integral contributions, which are essential for a self-consistent constitutive theory. Specifically, if relaxation functions like the shear and bulk modulus, coefficient of thermal expansion, and heat capacity are functions of temperature or specific volume significant double integral contributions appear. In particular, the temperature dependence of the heat capacity affects the nonequilibrium entropy; moreover, if an Adam-Gibbs relationship is postulated to describe how the log a shift factor depends upon the thermodynamic, these extra contributions can significantly affect the relaxation response in the glass. The predictions of the constitutive equation including all single and double integral contributions will be compared with a wide variety of nonlinear experimental data for an amine cured epoxy resin.

Symposium EX
New Experimental Methods

Organizer: Rangaramanujam M. Kannan

Tuesday 1:30 Los Angeles EX1

A NOVEL METHOD TO DETERMINE THE COMPLEX VISCOELASTIC COEFFICIENTS OF ULTRA-THIN FILMS

Chris C. White and Wen-Li Wu
Polymers Divsion, NIST, Gaithersburg, Maryland 29899

Recent experimental results based on x-ray reflectivity, ellipsometry and other techniques have demonstrated that the apparent physical properties of polymer films thinner than one micron may deviate significantly from the expected bulk values. The mechanical properties of the ultra-thin films (sub-micron) are experimentally difficult to determine with precision. The quartz crystal microbalance is an established technique for measuring the thickness of polymer thin films of a few microns thick, and in certain cases, qualitative viscoelastic data has been published. Recently, the quartz crystal microbalance technique has been highly modified for measuring the complex viscoelastic coefficients of sub-micron polymer films with high precision. The details and preliminary results from this technique will be presented.

Tuesday 1:55 Los Angeles EX2

NMRI INVESTIGATION OF SEDIMENTATION OF CONCENTRATED SUSPENSIONS IN NON-NEWTONIAN FLUIDS

Serge Bobroff and Ronald J. Phillips
Dept. of Chemical Engineering and Materials Science, University of California - Davis, Davis, California 95616

Nuclear Magnetic Resonance imaging (NMRI) is used to study rates of sedimentation in several non-Newtonian fluids. It is shown that either shear thinning or elasticity in a fluid can result in a time-dependent sedimentation rate, as measured by the motion of the suspension-supernatant interface. Sedimentation is most rapid at the beginning of the process, and grows steadily slower in time. Two dimensional images of vertical sections of suspension show clearly the development of a non-homogeneous microstructure during sedimentation in a viscoelastic fluid. Elongated columns of particles form in the direction of gravity, and these columns are separated by comparably sized regions of pure fluid. Such structures are not present in sedimentation in Newtonian fluids, where the suspension microstructure is homogeneous for the duration of the process.

Tuesday 2:20 Los Angeles EX3

POINTWISE OBSERVATIONS FOR RHEOLOGICAL CHARACTERIZATION

Robert L. Powell[1], Alireza Shekarriz[2], Darren Arola[3], Geoffrey Barrall[4], and Michael McCarthy[5]

[1]Chemical Engineering / Materials Science, University of California, Davis, CA 95616; [2]Battelle Pacific Northwest Laboratory, Richland, WA; [3]MBA Polymers, Richmond, CA; [4]Quantum Magnetics, San Diego, CA; [5]Food Science and Technology, University of California, Davis, CA

Results are presented for the use of pointwise methods to characterize the rheological properties of fluids. The most developed method is nuclear magnetic resonance imaging (NMRI). We present results which show the potential of this technique to determine the shear viscosity - shear rate relation ship over nearly two decades of shear rate from a single NMRI - pressure drop measurement. The effect of the experimental parameters on the accuracy and the measurement window will be discussed. A second technique, ultrasonic do ppler velocimetry (UDV) will also be described. This technique, or some variant thereof, has been used for velocity measurements in other applications and for some rheological characterizations. Results will be presented for the velocity profiles measured in Newtonian and a non-Newtonian fluids. In the latter case, the measured profiles will be compared with predictions based on independent rheological measurements. These show that UDV has potential similar to NMRI. Areas where more development would increase the accuracy of the data will be indicated.

Tuesday 2:45 Los Angeles EX4

DYNAMIC DEFORMATION VISUALIZATION IN SWELLING OF POLYMER GELS

E.C. Achilleos[1], Robert K. Prud'homme[1], K.N. Christodoulou[2], K.R. Gee[3], and K.R. Kevrekidis[1]

[1]Dept. Chemical Engineering, Princeton University, Princeton, NJ; [2]Avery, Inc., Pasadena, CA; [3]Molecular Probes, Inc., Eugene, OR

An optical technique for the real-time visualization of deformation in transparent gel processing is developed. The technique is based on copolymerizing in the gel a photoactivated fluorophore (PAF) chemically anchored on a monomer. A material grid is written using a UV-laser beam that uncages the fluorophore, and the (fluorescent) grid is visualized through an Ar-Ion laser sheet. We use this technique to monitor the swelling of constrained geometry polyelectrolyte gels (sodium polyacrylate and polyacrylamide) in salt solutions. Transient deformation and concentration fields are obtained, which, if coupled with constitutive equations, can be used to extract transient stress profiles in the gels.

Tuesday 3:35 Los Angeles EX5

A COMPRESSIONAL RHEOMETER FOR VISCOELASTIC FLUIDS

Peter R. Whittingstall[1] and William E. VanArsdale[2]

[1]TA Instruments Inc., New Castle, DE 19720; [2]Mechanical Engineering, University of Houston, Houston, TX 77204-4792

We describe the development of a novel compressional rheometer. This instrument uses a translational motor to oscillate a circular disk relative to a fixed surface. This oscillatory squeeze flow between parallel plates is used to obtain viscoelastic properties. The constrained material alters instrument response through a force on the moving disk. This force is known for small amplitude oscillations of a viscoelastic fluid through an analysis based on a lubrication approximation. This analysis is extended to larger gaps using known results for Newtonian fluids. Measurements are compared to viscoelastic data from a commercial rotational instrument.

Tuesday 4:00 Los Angeles EX6

REAL TIME ASSESSMENT OF THE RHEOLOGICAL BEHAVIOR OF POLYMERIC SYSTEMS DURING EXTRUSION

João M. Maia, José A. Covas, João M. Nóbrega, Ana V. Machado, and Olga S. Carneiro
Department of Polymer Engineering, University of Minho, 4800 Guimarães, Portugal

On-line measurements of the rheological properties of complex materials during processing have been hindered by a number of practical difficulties such as those related with sample collection and testing conditions. The former is normally done only at the end of the plasticization unit and, therefore, offers no information about the kinetics of the process. The latter is related with the delay between sample collection and testing and its implications in terms of material properties, e.g., it does not take into account possible coalescence in multi-phase materials or chemical conversion in reactive ones.

In the present work, an on-line capillary rheometer concept that attempts to minimize the above shortcomings, allowing material to be collected along a twin-screw extruder and tested within seconds is proposed. The instrument uses an in-house built sampling device, as well as a commercially available portable controlled-stress rotational rheometer. The sampling device allows the sample to be collected into the reservoir of the apparatus, on top of which the rotational rheometer is attached. The rotational motion of the latter is converted to a downward one, thus allowing a piston to be driven down and push the material through a die located at the bottom of the reservoir.

Instrument validation was performed off-line using several known-viscosity Silicone oils and on-line with two polymer melts (these last results being compared with data obtained from conventional rotational and capillary techniques). Experiments performed on complex systems included the monitoring of polymer degradation during extrusion, fiber degradation during the processing of carbon-fiber composites and reaction kinetics of materials obtained by reactive extrusion.

Tuesday 4:25 Los Angeles EX7

THE EFFECT OF PRESSURE ON THE VISCOELASTIC PROPERTIES OF A LLDPE

Francois A. Koran and John M. Dealy
Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

A new high-pressure rheometer has been developed to investigate the effect of pressure on the flow behavior of polymer melts. It uses a sliding plate geometry to generate a uniform plane Couette flow and measures the resulting shear stress locally at the center of the sample. This design eliminates the inhomogeneities in strain and pressure that occur in high pressure capillary and slit rheometers, thus producing correction-free results. While this is important for determining steady state rheological properties, it is critical for measuring transient rheological properties. As a result, it is now possible to investigate the effect of pressure on viscoelasticity. Flows of interest include oscillatory shear, step strain, creep recovery, and exponential shear. The new rheometer was used to determine the effect of pressure on the viscoelastic properties of a linear low density polyethylene. Results are presented for experiments performed at 175°C and for pressures ranging from atmospheric to 10,000 psi.

Tuesday 4:50 Los Angeles EX8

NEW APPROACH IN MEASURING LOW FREQUENCY VISCOELASTIC PROPERTIES

Edwin Matthew C. Cua[1] and Montgomery T. Shaw[2]
[1]Polymer Program, University of Connecticut, Storrs, CT 06269-3136; [2]Dept. of Chemical Engineering & Inst. of Material Science, University of Connecticut, Storrs, CT 06269

The measurement of linear viscoelastic properties at very low frequencies has been a long-standing problem for polymers with temperature shift factors close to unity, e.g. polyethylene. Considerable interest in determining these properties arise because they control the elastic behavior of melts and solutions. Access to these long time scales present an experimental challenge in terms of stability and resolution using commercial instruments without tying the equipment up for a long time. We are currently devising a set-up where measurement in vacuum of long-time creep is possible using a novel but simple optical system. The system employs interference rings which has a resolution of a quarter of the wavelength of the light source. With low cost, many test units can be run simultaneously.

Wednesday Morning

Symposium PL
Plenary Lectures

Wednesday 8:30 Steinbeck Forum PL3

INTERFACIAL RHEOLOGY OF SIMPLE LIQUIDS AND POLYMERS

Steve Granick
Materials Sci. and Engineering, University of Illinois, Urbana, IL 61801

A picture is emerging of how and why interfacial rheology of fluids differs from that in the bulk. Measurements directed to this end have been carried out with a surface forces apparatus that was modified to perform dynamic mechanical experiments over a wide range of strain, from linear response (sub-angstrom deformations) to strongly nonlinear. The viscoelastic spectrum is found to be retarded relative to the bulk with the result that prominent elastic phenomena intervene even for fluids that in the bulk would be Newtonian. This may be the manifestation of collective motions, possibly reflecting enhanced entanglement interactions. It is possible in the thin-film geometry to achieve strains in dynamical oscillatory experiments that far exceed unity and in this way to explore the limiting rheological response at very large deformation. Here we find saturation of the viscous stress at a limiting value (which is pertinent to the stick versus slip boundary conditions) and giant fluctuations of the viscoelastic response that nonetheless show statistical regularity. The fascinating commonalities between the rheological responses of the present systems and glasses, dense colloidal suspensions, and granular materials will be discussed.

Symposium SE
Suspensions and Emulsions

Organizers: Norman J. Wagner and Robert J. Butera

Wednesday 9:45 San Carlos I SE1

DEFORMATION OF A VISCOELASTIC DROP IN THE FLOW INDUCED BY A POTENTIAL VORTEX

Kausik Sarkar and W. R. Schowalter
Chemical Engineering, University of Illinois, Urbana, IL 61801

Earlier work has shown that important features of fluid response are revealed in the flow of a potential vortex. Vortex-type flow provides an interesting alternative to the more traditional shear/extensional flows associated with the four-roll mill.

We have performed calculations for a viscoelastic drop immersed in a viscous fluid subjected to a vortex-type flow. Time dependent evolution of the drop shape is followed. From the results one can infer drop response in turbulent flows characterized by vortex strength.

Computations are performed at small but non-zero Reynolds numbers using a front tracking/finite difference method developed by Tryggvason. The method was enhanced to allow for a Maxwell model constitutive equation. The relaxation time is distributed in a narrow region near the surface and varies from the value in the interior of the drop (λ) to zero. A scheme is developed in which an analytical integration is followed by discretization. The effect of λ on evolution of drop shape is shown.

Wednesday 10:10 San Carlos I SE2

RHEOLOGICAL PROBING OF THE MORPHOLOGY DEVELOPMENT IN IMMISCIBLE BLENDS DURING FLOW REVERSAL

Paula Moldenaers, Mario Minale, and Jan Mewis
Chemical Engineering Department, K.U. Leuven, Leuven 3001, Belgium

The rheological and morphological behaviour of viscous emulsions or uncomptabilized polymer blends in simple flow conditions is rather well understood. Here, more complex flows are explored. For this purpose flow reversal has been selected. More specifically the flow was reversed after the sample had been subjected to a sudden increase in shear rate. Transient normal stresses have been used to probe the morphological changes.The samples consisted of semi-concentrated mixtures of immiscible polymers that were liquid at ambient temperature, i.e. poly(isobutene) and poly(dimethylsiloxane). In the concentration range used the blends had a droplet-matrix structure. Two different types of response could be distinguished during flow reversal, depending on whether the droplets broke up or not before the flow was reversed. Without break-up the transient stresses resemble those during the preceding step-up experiment. Once break-up has occurred longer and more complex transients are recorded. Assuming that the droplets deform affinely and using Batchelor's expression for the stress, the data can be modeled, at least qualitatively. The interfacial stresses, however, introduce some degree of irreversibility which results in a residual mean stretching of the droplets that persists throughout the flow reversal. This is confirmed by light scattering and dichroism measurements during flow.

Wednesday 10:35 San Carlos I SE3

DEFORMATION OF A SINGLE FLUID DROP IMMERSED IN A SECOND MOVING FLUID: EXACT MATHEMATICAL RESULTS FOR SLOW FLOWS

Francesco Greco
Chemical Engineering Department, University of Naples "Federico II", Naples 80125, Italy

In this presentation, the problem of determining the 3D-shape of a fluid drop immersed in a second fluid flowing in a prescribed way at infinity is discussed from a theoretical point of view. The standard analytic approach to the problem via balance equations is heavily burdened by the fact that a part of the boundary conditions to be satisfied (matching of inner and outer velocities, balance of pressures also accounting for surface tension, etc.) is assigned on the surface of the deformed drop, which is itself unknown. As a consequence of this intrinsic mathematical difficulty, almost all of the available literature on this subject only deals with the constitutively simplest case, namely, the one with two Newtonian fluids. Explicit results have been obtained in the limit of slow flows, as reviewed by Rallison some years ago (J.M.Rallison, J.Fluid Mechanics, 98 (1980) 625).

Here, we tackle the problem in a completely new way. Without solving or even writing down balance equations, we show that the shape of the deformed drop can be determined unambiguously for any kind of slow flow at infinity by an elementary application of a well known mathematical theorem (C.Truesdell, W.Noll, in Handbuch der Physik, Vol.III/3 (1965), S.Flugge Ed., Springer Verlag). Because there is no hypothesis on the constitutive nature of the component fluids, the result is rather general. On the other hand, as it always is for a continuum mechanics approach, the relevant formulae contain phenomenological coefficients which should be experimentally determined. We will also discuss here how these coefficients can be measured in a simple flow field (shear flow).

Wednesday 11:00 San Carlos I SE4

RELATIONSHIP BETWEEN MORPHOLOGY AND ELASTIC RECOVERY IN IMMISCIBLE BLENDS

Inge Vinckier, Paula Moldenaers, and Jan Mewis
Chemical Engineering Department, K.U. Leuven, Leuven 3001, Belgium

It has amply been demonstrated in literature how mainly the elastic properties of immiscible blends reflect their underlying morphology. The recovery after shear flow, although it is also a measure of elasticity, has attracted only limited attention so far. The aim of this study is twofold: recoil measurements will be used as a probe for the underlying morphological processes and it will be attempted to predict the elastic recovery, or at least its scaling behaviour. A systematic set of experimental data on recovery of semi-dilute immiscible blends, after both a steady state and a transient shear history, is obtained. The shape relaxation of the disperse phase shows up in both the level and the time scale of the recovery. The elastic recovery caused by a slightly deformed structure can be described quantitatively by the Palierne model, when the size of the disperse phase is known. However, the retardation time should modified to account for the aspect ratio of the droplet phase. Additionally, it has been demonstrated that a particular scaling relation for recovery curves can be derived from the Doi-Ohta theory. This scaling property is indeed reflected in the experimental recovery curves.

Wednesday 11:25 San Carlos I SE5

EVOLUTION OF RHEOLOGICAL PROPERTIES DURING THE FORMATION OF AN EMULSION OF INK AND FOUNTAIN SOLUTION

Suresh Mani[1], Jennifer Jensen[2], and William Lim[1]
[1]Physical Sciences Lab, Flint Ink Research Center, Ann Arbor, MI 48105; [2]Chemical Engineering, University of Michigan, Ann Arbor, MI

In offset lithography an oil-based printing ink comes in contact with a water-based fountain solution and the interactions between the two phases or "ink-water balance" strongly influences the print quality (Fetsko, 1986). The success of several studies, e.g., Palierne, (1990) in relating the microstructure and interfacial tension of polymer blends and emulsions to their rheological properties has motivated the present work.

Emulsions of a commercially available paste (heatset) ink and a fountain solution were studied as a function of the volume fraction of fountain solution (FS); inks themselves are filled systems consisting of pigments in a polymer solution, showing shear thinning, thixotropy, and elasticity, e.g., Mani et al. (1996). The low shear (0.005 to 5 s-1) viscosity of the emulsions are significantly larger than the viscosity of the inks; emulsions containing the smallest volume fraction (approximately 5%) of FS had the highest viscosity. Low frequency G' values of all emulsions were significantly larger than G' values of the inks; the increase in G' was the greatest at low concentrations (approximately 5%) of FS. A combination of fluorescence and optical microscopy showed that the emulsions with 5% FS had a mean droplet size of 30 microns, whereas emulsion with 20% FS had a mean droplet size of 14 microns.

Symposium CF
Coupling Flow and Order in Fluids

Organizer: Lynn Walker

Wednesday 9:45 San Carlos III CF9

DIRECT NUMERICAL DYNAMIC SIMULATION OF NEMATIC DEFECT STRUCTURES IN RECTILINEAR SHEAR FLOW

Tomohiro Tsuji[1], Alejandro D. Rey[2], and Shigeomi Chono[1]
[1]Department of Intelligent Mechanical System Engineering, Kochi University of Technology, Kochi 7820003, Japan; [2]Department of Chemical Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

The dynamical behavior of nematic defect structures in rectilinear shear flow has been simulated using a tensor order parameter model that takes into account short range and long range nematic order, and visouc flow effects. The defect structures are self-selected and arise through the isotropic-nematic phase transition. The well-known defect coarsening process of the defect structures is observed and characterized both in the presence and in absence of shear flow. The effect of shear flow is to accelerate the coarsening process, and the law of defect interaction are different from that without shear flow. It is found that higher order defect structures can arises from the coupled effects of shear flow and anchoring conditions. Rheological properties of liquid crystalline materials with defects will also be discussed.

Wednesday 10:10 San Carlos III CF10

ELONGATION-INDUCED BIAXIAL PATTERNS AND INSTABILITIES

Greg Forest[1] **and Qi Wang**[2]

[1]Mathematics, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3259; [2]Mathematical Sciences, Indiana University, Purdue University at Indianapolis, Indianapolis, Indiana 46202

A Doi-type model for flows of liquid crystalline polymers (LCPs) is applied to study the orientation response to imposed simple elongation. The flow stretches either along an axis of symmetry or in the plane orthogonal to it. A full biaxial orientation tensor is employed in the Doi nematodynamic equations, complementing earlier results of See, Doi, Larson (1990), Bhave, Menon, Armstrong, and Brown (1993), and Rey (1995). We describe the following results: (i) homogeneous and axisymmetric biaxial patterns exist in response to both types of simple elongation; (ii) a complete phase diagram is given in the two-parameter space of LCP concentration and elongation rate; (iii) the linearized Doi model is exactly solved about all equilibrium patterns, revealing all co-existing stable states for each concentration and flow rate; (iv) new biaxial instabilities are revealed, residing not only in order parameters of the orientation tensor, but also in the nematic directors! For example, we deduce that beyond a moderate LCP concentration, and for arbitrary planar elongation rate, the only stable orientation patterns are biaxial. In contrast, for elongation that stretches along the flow axis of symmetry, biaxial states exist but they are all unstable. These predictions suggest very different orientation techniques and data need to be collected to fully resolve the flow-induced order in unidirectional versus planar stretching flows.

Wednesday 10:35 San Carlos III CF11

SIMULATIONS OF TEXTURED LIQUID CRYSTALLINE POLYMERS IN SHEAR FLOWS

Mark N. Kawaguchi[1]**, Raz Kupferman**[2]**, and Morton M. Denn**[1]

[1]Materials Sciences Division/Dept. Chemical Engineering, Lawrence Berkeley Nat. Lab. & U. California at Berkeley, Berkeley, CA 94720-1462; [2]Mathematics Department, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

We present a model of textured liquid crystalline polymers within the context of an orientationally-averaged Doi theory. The addition of the Marrucci and Greco potential [1] incorporates the effects of long-range interactions, from which the corresponding orientation equations and stress tensor are derived. We have carried out flow simulations for three cases of increasing complexity: spatially-homogeneous simple shear flow with decoupled orientation and velocity fields, 1-D spatially-varying simple shear flow with decoupled orientation and velocity fields, and 1-D spatially-varying shear flow with fully-coupled orientation and velocity fields. The orientation and velocity fields for the fully-coupled cased are qualitatively different from those for the uncoupled simulations, with steady-state texture developing only with full coupling.

[1] G. Marrucci and F. Greco, Mol. Cryst. Liq. Cryst. 206, 17 (1991).

Wednesday 11:00 San Carlos III CF12

A CONTINUUM MODEL FOR FLOW-INDUCED CRYSTALLIZATION OF POLYMER MELTS

Anthony J. McHugh, Antonios K. Doufas, and Issam S. Dairanieh

Chemical Engineering, University of Illinois, Urbana, IL 61801

We have developed a macroscopic continuum model for flow-induced crystallization (FIC)based on the Hamiltonian/Poisson Bracket formalism combined with the Avrami equation. The model has been used to simulate FIC of polymer melts in homogeneous, isothermal flow fields. The model predicts crystallization kinetics as well as rheological and rheo-optical behavior of semi-crystalline systems. The amorphous phase is modeled as a modified Giesekus fluid and the crystalline phase as a collection of non-interacting, multi-bead rods that grow and orient in the flow field. The two phases are coupled with crystallinity via the dissipative Poisson brackets. Orders of magnitude reduction in induction times and enhancements in crystallization rates are predicted under flow as well as the appearance of critical deformation rates. Increases in system stiffness due to crystallization show in the stress deformation-rate behavior. For the temperature range studied, hydrodynamic forces dominate the undercooling effect. Model predictions compare very favorably with published experimental studies.

Wednesday 11:25 San Carlos III CF13

MOTION OF KINK BOUNDARIES IN LAYERED LIQUIDS

David C. Morse

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

Kink boundaries are non-topological planar defects that separate domains with different layer orientations in block copolymer lamellar phases and other Smectic A liquid crystals, as well as in strongly deformed layered solids such as sedimentary rocks. I will discuss the continuum mechanics of the motion of kink boundaries and kink bands, i.e., strips of misaligned material that are separated from an otherwise homogeneous material by pairs of kink boundaries. Analytic results are found for the rates of change of the orientation and width of a well-developed kink band in a homogeneously deforming material. It is found that the rate of shear (defined in terms of the difference between tangential velocities of neighboring layers) within such a band is always opposite to that in the surrounding material, and that, in simple shear flow, the band must experience a uniaxial tension, yielding an slight dilation of the layer spacing within the band.

Symposium SL
Rheology of Solids

Organizers: Andre Lee and Gregory B. McKenna

Wednesday 9:45 San Carlos II SL5

A MODIFIED TNM-KAHR MODEL FOR HYGROTHERMAL EFFECTS ON PHYSICAL AGING AND STRUCTURAL RECOVERY OF AN EPOXY THERMOSET

Won H. Han and Gregory B. McKenna

Polymers Division, NIST, Gaithersburg, MD 20899

Much work has already shown that the TNM-KAHR model of structural recovery provides a reasonable framework in which to describe temperature jump experiments in structural glasses. Here we extend the model to consider moisture uptake problems and demonstrate that the model can capture RH-jump results that mimic the classic asymmetry of approach and memory effects in T-jump experiments. We have investigated the hygrothermal effects on thin epoxy films (c.a. 50 µm thick) using mass uptake, swelling, and uniaxial creep compliance measurements inside a dew formation-free transparent chamber capable of arbitrary relative humidity and temperature controls. Volumetric response was determined as a function of relative humidity by constant humidity dilatometry under constant rate temperature cooling. Using constant temperature dilatometry, volume is determined as a function of temperature under constant rate of dehumidification. Similarly, volumetric measurements were performed after either T-jumps or RH-jumps and structural recovery measured. We also show that the physical aging behavior under humidity down-jumps is equivalent to temperature down-jump such that the time-aging time superposition principle holds for both cases.

Wednesday 10:10 San Carlos II SL6

SMALL-STRAIN CREEP AND AGING OF THERMOPLASTIC ELASTOMERS (TPE-E)

Reinhold Wimberger-Friedl and Hans de Bruin

Polym. & Org. Chem., Philips Research, Eindhoven 5656 AA, Netherlands

The small-strain creep of elastomers of the block- copolyether-ester type (TPE-E) is investigated and compared with that of poly-butylene-terephthalate (PBTP), the hard segment building block of the TPE-E, and liquid-crystalline aromatic polyester, LCP. The effect of annealing and aging is studied. It is found that non-annealed TPE-E shows a strong aging dependence even 100°C above the Tg of the soft phase, whereas the creep of annealed TPE-E becomes totally independent of aging, and composition within the investigated range and even independent of temperature at higher temperatures. The change upon annealing is explained by phase separation and crystallization. The creep compliance of annealed TPE-E can be described by a stretched-exponential equation with exponent 0.1. Whereas the creep and aging behavior of PBTP and LCP can be described by the model of Struik [1], the combination of a strongly temperature dependent initial compliance with an independent creep rate of the TPE-E is a peculiar behavior and not readily explained by microscopic models. Reference: 1. Struik, L.C.E. Polymer, 28, 1521, (1987)

Wednesday 10:35 San Carlos II SL7

MODELING OF MATERIALS SHOWING VISCOPLASTIC BEHAVIOR WITH NONLINEAR FRACTIONAL-ORDER DIFFERENTIAL EQUATIONS

Alan D. Freed[1] and Kai Diethelm[2]

[1]Materials Division, NASA Lewis Research Center, Cleveland, OH 44135; [2]Institut fur Mathematik, Universitat Hildesheim, Hildesheim D-31141, Germany

Internal state variable theory is used to demonstrate similarities and differences between viscoelastic and viscoplastic material models. The kinematics are for large deformations and are based on Biot's measures for stress and strain. Fractional-order, viscoelastic, material models have been around since the 1930's, and they constitute an important class of viscoelastic models. Cureously, the fractional calculus has not been applied to viscoplastic model development. This paper begins such a development process by examining the role that fractional-order evolution equations might play in viscoplastic material modeling.

To enable such a study to even exist in the first place requires a numerical technique capable of solving systems of nonlinear, fractional-order, differential equations, cast as initial-value problems. To complicate matters, this fractional system is coupled with a system of nonlinear, first-order, differential equations. There is no technique in existence today that can solve such an initial-value problem. Therefore, a second objective of this paper is to present the development of a numerical integrator that can handle systems of differential equations like these.

To investigate the applicability of fractional evolution in viscoplasticity, our numerical method is used to gain solutions to two types of boundary-value problems: the planar elongation of a solid in 1- or 2-D, and the tension\torsion\inflation of a thin-walled tube. The materials selected for modeling purposes include: PVC plastic, aluminum and copper. These model materials were selected because of the large amount of experimental data that exists for them in the literature.

Wednesday 11:00 San Carlos II SL8

COMPARISON OF THE VOLUME AND TEMPERATURE DEPENDENCE OF VARIOUS LOG A SHIFT MODELS WITH EXPERIMENTAL DATA

S. J. Lee, G. Medvedev, and J. M. Caruthers

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

The internal clock models (i.e. Schapery; Knauss-Emri; Lustig-Shay-Caruthers) are a class of constitutive models for describing the nonlinear viscoelastic behavior of polymer solids that are currently receiving considerable attention. The key nonlinearity in these models is a log a shift function or functional that defines how the rate of relaxation depends upon the current state of the system, where the various models use different relationships. Inherent in all the proposed models is the ability to capture the volume and temperature dependence of the shift function/functional. The log a shift function relationship is typically evaluated using data in the VT region along the P=1atm isobar; however, deformations of a glassy material generate changes in specific volume that explore a much larger VT region. Zero shear rate viscosity data is available over an extremely large temperature (100 oC) and pressure (0 to 5kbar) regions for a variety of small molecule and some polymeric glass formers. Using the viscosity data along with equilibrium PVT surfaces parameterized by a Tait equation, log a contours in the equilibrium/rubbery state are generated for a significantly larger region of the VT space than is traditionally considered. When the data is extrapolated to slightly negative pressures (i.e. an equal triaxial extension), the iso-log(a) lines exhibit an unanticipated maximum in VT space. At low temperatures the slope of the iso-log(a) line is consistent with simple free volume ideas, while at high temperatures the slope is consistent with configurational entropy or pressure modified free volume ideas; however, none of the existing log a models is able to capture both the low and high temperature behavior. We are currently examining if Adam-Gibbs like models that include second order effects in the configurational entropy, free energy etc. can capture the maximum in the iso-log(a) behavior.

Wednesday 11:25 San Carlos II SL9

VISCOELASTIC RESPONSES OF NANO-CLUSTER REINFORCED POLYMERS

Andre Lee

Materials Science and Mechanics, Michigan State University, E. Lansing, MI 48824

Recently, families of functionalized polyhedral oligomeric silsesquioxane (POSS) macromers bearing epoxide groups have been developed. This paper presents an investigation of the thermal and viscoelastic property enhancements in commonly used epoxies reinforced with mono-functional POSS-epoxy macromers. Glass transitions of these POSS-epoxy nano-composites were studied using differential scanning calorimetry. Small strain stress relaxation under uniaxial deformation were examined to provide insights into the time-dependent viscoelastic behavior of these nano-composites. The POSS-epoxy macromers utilized in this study were mono-functional and hence occupied chain terminus points within the network. Nevertheless, they were effective at hindering the molecular motion of the epoxy network junctions. Thus the glass transition temperature, Tg, was observed to increase with increasing weight fraction of the mono-functional POSS-epoxy. The viscoelastic response at temperatures below Tg was examined and was found to correlate to a stretched exponential relaxation function. Time-aging superposition was found to be applicable to the data under all test conditions and for all of the materials used in this study. Surprisingly, the instantaneous modulus was not observed to be effected by incorporation of the POSS nano-reinforcement. This suggests that while POSS cages influence polymer chain motions, including the motion of the molecular junctions, these nano-reinforcements did not participate in the overall deformation of the chains. Experiments performed under identical thermodynamic states, revealed that the molecular level reinforcement provided by the POSS cages also retarded the physical aging process in the glassy state. Therefore, the time required to reach structural equilibrium was longer for samples reinforced with POSS-epoxy than for those of the neat resins.

Symposium AN
Analytical and Numerical Solutions to Flow Problems

Organizer: Michael Renardy

Wednesday 9:45 Los Angeles AN1

STABILITY AND NONLINEAR DYNAMICS OF VISCOELASTIC SHEAR FLOWS SUBJECTED TO SECONDARY FLOW

Venkat V. Ramanan, K. A. Kumar, and Michael D. Graham

Department of Chemical Engineering, University of Wisconsin-Madison, Madison, WI 53706

We investigate the effect of superposition of a time-periodic axial Couette flow on the viscoelastic circular Couette and Dean flow instabilities. The analysis, carried out for the Oldroyd-B fluid, generally shows increased stability as compared to when there is no axial flow. However, in the circular Couette case, the flow shows instability - synchronous resonance - for some parameter values. Two general regimes of instability are observed, one when the forcing frequency is close to the inverse of the polymer relaxation time and, surprisingly, another when the frequency is much lower. In the latter regime, the disturbances display quiescent intervals punctuated by periods of large transient growth and subsequent decay. Asymptotic and numerical results indicate that the high frequency, low axial Weissenberg number regime is essentially equivalent to the case without axial flow, implying no stabilization, while at high values of frequency and axial Weissenberg number, the flow is always stable. Consistent with previous results on parametrically forced systems, the zero frequency limit is singular.

We also present stability results for the addition of steady axial Couette and Poiseuille flows to viscoelastic instabilities in azimuthal Dean flows. The qualitative effect of adding a steady axial flow is similar to that of the circular Couette geometry for high axial Weissenberg number, with the critical azimuthal Weissenberg number increasing linearly with the axial Weissenberg number. For low axial Weissenberg number, the flow is stabilized, in

constrast to the circular Couette flow. Weakly nonlinear analysis shows that the criticality of the bifurcation depends on the values of axial Weissenberg number and solvent viscosity. Finally, we also show the presence of a codimension-2 Takens-Bogdanov bifurcation point in the linear stability curve of Dean flow. This point represents a transition from one mechanism of instability to another.

Wednesday 10:10 Los Angeles AN2

STABILITY OF VISCOELASTIC TAYLOR-COUETTE FLOW: INFLUENCE OF RELAXATION SPECTRUM AND ENERGETICS

Usamah A. Al-Mubaiyedh, R. Sureshkumar, and Bamin Khomami
Chemical Engineering, Washington University, St. Louis, MO 63130

The stability of viscoelastic Taylor-Couette flow has been a subject of numerous investigations in the last decade, demonstrating the existence of purely elastic instabilities in this flow (Shaqfeh, Annual. Rev. Fluid Mech., 1996). However, linear stability analysis using single mode, quasilinear constitutive equations overpredict the onset Deborah number as compared to that observed experimentally. Moreover, for values of elasticity number E, defined as the ratio of Deborah and Reynolds numbers, exceeding 0.01 and for relatively narrow gaps, linear stability analysis predicts doubly degenerate non-axisymmetric Hopf bifurcations (Avogousti and Beris JNFM 1993) and, the nonlinear analysis has shown the bifurcations to be subcritical (Sureshkumar et. al. Proc. R. Soc. London. 1994). Whereas this observation seems to be supported by experiments in the inertial regime (Groisman et. al., Phys. Rev. Letters 1996), the primary flow transitions observed for order one or larger values of E are axisymmetric and steady (Baumert and Muller, Phys. Fluids 1996). Among the various factors which could alter the stability characteristics are the presence of a spectrum of fluid relaxation times and non-isothermal effects caused by viscous dissipation. In this study, we examine the stability of the Taylor-Couette flow utilizing realistic non-linear multimode differential constitutive equations. In addition, using thermodynamically consistent constitutive equations constructed for thermo-rheologically simple fluids (Crochet and Naghdi, J. Rheol., 1987), the influence of non-isothermal rheology on the stability of the Taylor-Couette flow is explored. Results will be presented to elucidate how the aforementioned considerations modify the onset conditions, structure of the eigenspectrum and the spatial and temporal characteristics of the secondary flow. The results will be compared with available experimental observations.

Wednesday 10:35 Los Angeles AN3

STABILITY ANALYSIS OF THE ECCENTRIC DEAN FLOW OF AN UPPER CONVECTED MAXWELL FLUID

R. Sureshkumar[1] and Marios Avgousti[2]
[1]Chemical Engineering, Washington University, St. Louis, MO; [2]Polymer Research and Development, Union Carbide, Somerset, NJ 08875

Stability analysis of periodically constricted viscoelastic flows presents a challenging problem relevant to polymer processing industry, polymeric flow through porous/fibrous medium and viscoelastic flow modeling. In this work, we investigate the stability of a viscoelastic flow between eccentric cylinders, driven by either an imposed constant pressure gradient in the azimuthal direction (viscoelastic eccentric Dean problem) or a combination of the rotation of the cylinders and an imposed pressure gradient (viscoelastic eccentric Taylor-Dean problem). The base flow solution for the eccentric Dean (ED) and the eccentric Taylor-Dean (ETD) geometries are evaluated numerically using a pseudo-spectral collocation technique which employ Chebyshev and Fourier basis functions in the radial and azimuthal directions, respectively. The stability of the base flow is then investigated by solving a generalized, complex eigenvalue problem resulting from the linearized set of governing equations. The eigenfunctions are represented by Chebyshev and Fourier expansions in the inhomogeneous radial and azimuthal directions, respectively. Due to the large sizes of the matrices involved, Arnoldi iterations are used to selectively evaluate the most dangerous eigenvalues. Code validation is done by comparing the results for the onset conditions at vanishingly small eccentricity and sufficiently narrow gap with those obtained for the Dean and the Taylor-Dean flow by Joo and Shaqfeh (1992). Results will be presented to elucidate the structure of the eigenspectrum, the critical eigenfamilies and onset conditions and the structure of eigenfunctions and their dependence on eccentricity and gap width. Potential mechanisms which cause the modification of the stability boundary of the Dean flow by the periodic geometric modulation due to the eccentricity will be discussed.

Wednesday 11:00 Los Angeles AN4

SWIRLING FLOW OF VISCOELASTIC FLUIDS: INTERACTION BETWEEN INERTIA AND ELASTICITY

Jason R. Stokes[1], Nicholas J. Lawson[1], David V. Boger[1], and L.J.W. Graham[2]
[1]Chemical Engineering, University of Melbourne, Parkville, Victoria 3052, Australia; [2]Building, Construction and Engineering, CSIRO, Highett, Victoria 3190, Australia

The secondary flow behavior of liquids in an enclosed cylindrical vessel containing a rotating base (or lid) provides a complex flow field where the boundary conditions are precisely specified and axial symmetry can be maintained with good accuracy. Hence, confined swirling flow in the disk and cylinder system provides a good test case for comparison with numerical studies for the flow of elastic liquids. Swirling flows are also extremely common throughout process engineering applications and therefore an understanding of the fundamental behavior of non-Newtonian liquids under swirl is industrially relevant. The behavior of dilute flexible and semi-rigid polymer solutions with a constant viscosity in confined swirling flows is investigated. Constant viscosity elastic liquids, commonly referred to as Boger fluids, are used to ensure that the changes in the flow kinematics are associated purely with fluid elasticity and cannot be confused with shear thinning viscosity which is found in all previous experimental works using non-Newtonian fluids in confined swirling flow.

In this paper results of the investigation compare vortex breakdown for low viscosity Newtonian inelastic liquids to low viscosity elastic liquids where a complex interaction between inertia and elasticity is observed.

Wednesday 11:25 Los Angeles AN5

STABILITY ANALYSIS OF COMPLEX VISCOELASTIC FLOWS USING TIME DEPENDENT SIMULATIONS

Bin Yang and Bamin Khomami
Department of Chemical Engineering, Washington University, St. Louis, MO 63130

Viscoelastic instabilities most often are the limiting factor in enhanced production of polymeric and polymeric based composite materials. To date, the analysis of viscoelastic instabilities has been mostly limited to linear stability calculations in simple rectilinear flows where direct eigenvalue solvers can be used to analyze the stability of the system. Such an approach is not feasible for analyzing the stability of 2D and 3D flows due to the tremendous cost associated with the simulations. In this study, we have used our recently developed higher order finite element techniques for simulation of steady and transient viscoelastic flows to analyze the effect of fluid elasticity on the stability of two industrially significant flows, namely, flow past periodic arrays of cylinders as well as flow in contractions. Specifically, the stability of both flows to 2D and 3D periodic disturbances has been studied using quasilinear constitutive equations such as the Oldroyd-D and the upper-convected Maxwell models as well as the multi-mode Giesekus model. Based on these studies we have identified the critical Deborah number for the onset of the instability as well as examining the effect of multiple modes of relaxation time on the onset conditions and the full nonlinear development of the instability. In turn, the results of our analyses are compared with prior experimental results and it is shown that the simulations are capable of predicting the experimentally observed instabilities with reasonable accuracy.

Wednesday Afternoon

Symposium SE
Suspensions and Emulsions

Organizers: Norman J. Wagner and Robert J. Butera

Wednesday 1:30 San Carlos I SE6

DROPLET COALESCENCE IN THE SHEAR FLOW OF MODEL EMULSIONS

Adam Al-Mulla and Rakesh K. Gupta

Chemical Engineering, West Virginia University, Morgantown, WV 26506

Morphology evolution during the shear flow of an immiscible blend of castor oil dispersed in a matrix of silicone oil is examined; an ultrasonic device is used to emulsify the liquids. The two densities are essentially the same, and it is verified that the emulsion is stable for at least two days. Droplet coalescence, however, occurs due to shear-flow-induced collisions, but droplet break-up is prohibited since the ratio of the dispersed phase viscosity to the continuous phase viscosity is 15.5. Shearing experiments are conducted in a cone-and-plate instrument and also in tubes of varying length. Dispersed phase concentrations up to 5%, two temperatures, and a variety of shear rates up to 50 reciprocal seconds are examined. The average droplet size is obtained with the help of optical microscopy as a function of the time of shearing till a steady state in the size is achieved. These results are compared to those of others and also to the predictions of available theories. An unusual finding is that coalescence does not occur if the initial droplet size is small and uniform across the sample; droplets merely stick to each other and maintain their separate identity.

Wednesday 1:55 San Carlos I SE7

SHEAR MODULUS OF A DRY SOAP FROTH WITH RANDOM STRUCTURE

Andrew M. Kraynik[1] and Douglas A. Reinelt[2]

[1]Department 9112 MS0834, Sandia National Labs, Albuquerque, NM 87185-0834; [2]Department of Mathematics, Southern Methodist University, Dallas, TX 75275-0156

We analyze the microrheology of a dry soap froth with random cell structure. The jammed state causes solid-like response under static conditions where energy minimization determines foam geometry. All of the foam structures that we describe are calculated with the Surface Evolver, a computer program developed by K.A. Brakke. The relationship between macroscopic stress and microscopic, cell-level geometry will be emphasized. Dry foams, which contain negligible liquid, satisfy Plateau's laws: polyhedral cells are separated by surfaces with constant mean curvature; three faces meet at equal dihedral angles along each cell edge; and four edges meet at each cell vertex at the tetrahedral angle. Random foams are derived by minimizing the surface area of Voronoi partitions of space; various algoriths are used to produce Voronoi seeds. Geometrical features relating to foam topology, surface area, edge length, and bubble pressure will be compared. We will focus on the shear modulus of dry foams with different cell-size distributions. We compare and contrast these results with the behavior of Kelvin and tetrahedrally close-packed (TCP) foams, which have crystal symmetry, as well as predictions based on 2D models.

This work performed at Sandia National Labs with support from the U.S. Department of Energy under contract DE-AC04-94AL85000 and from the Dow Chemical Company under a CRADA.

Wednesday 2:20 San Carlos I SE8

VISCOELASTICITY OF DISPERSIONS CONTAINING ASSOCIATIVE POLYMERS

Quynh T. Pham[1], William B. Russel[1], Jack T. Thibeault[2], and Willie Lau[2]
[1]Chemical Engineering, Princeton University, Princeton, NJ 08544; [2]Research Laboratories, Rohm and Haas Company, Spring House, PA 19477

Hydrophobically-modified water-soluble polymers of a triblock or telechelic structure form associated solutions of enhanced viscosity and viscoelasticity. Addition of the polymers to aqueous latex dispersions produces rheological properties greatly different from those of the neat dispersions. Our objective is a quantitative mechanistic model of the rheology, incorporating interactions between latices and polymers. These are PMMA particles and linear PEO endcapped with alkane hydrophobes. Adsorption isotherms and layer thicknesses are readily measured for dilute concentrations of polymers and latices via centrifugation and dynamic light scattering. The polymers adsorb on latices via hydrophobic interactions to generate dense layers that increase the particle hydrodynamic size but also reduce the polymer concentration in solution, thereby decreasing the continuum viscosity. Moreover, our results suggest that the polymers adsorb with one hydrophobe on the latice and the other free to couple with polymers in solution and adsorbed layers on other particles.

Measurements of steady shear viscosity and viscoelastic moduli characterize the rheology over full ranges of dispersion and polymer concentrations. The observed enhancement of the dispersion viscosity arises from the high viscosity of the polymer solution, the increased hydrodynamic volume of the particles, and direct interactions between adsorbed layers. Similarly the linear viscoelasticity of the dispersions reflects both the effect of the polymer continuum and the nature of the interactions of the particles with the polymer and among themselves. The loss and storage moduli fit the Maxwell model for a single relaxation time elastic fluid at high frequencies; however, the behavior at low frequencies is intermediate between that of a liquid and a solid. This information will be interpreted via extant theories for the configuration of adsorbed layers and the forces transmitted between the coated particles.

Wednesday 2:45 San Carlos I SE9

RHEOLOGY AND MICROSTRUCTURE OF SHEARED ARRAYS OF COLLOIDAL PARTICLES

Jeffrey J. Gray and Roger T. Bonnecaze
Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712-1062

Concentrated suspensions of colloidal particles undergo dynamical microstructural transitions under shear. During the transition from oscillating face-centered cubic twin structures to sliding layer structures, the system can exhibit hysteretic and discontinuous rheology as the shear rate is varied. We capture this behavior with a dynamic simulation of a sheared lattice of non-Brownian spherical particles with screened electrostatic interactions and hydrodynamic interactions determined using the Stokesian dynamics approximation. Rheological data are determined for a range of volume fractions, electrostatic screening lengths and shear rates or shear stresses. In controlled stress simulations, static yield stresses are observed. In controlled shear rate simulations of certain lattice orientations, plateau viscosities are observed at high and low shear rates with a high to low shear rate plateau viscosity ratio ranging from 1.4 to 2.2. Large viscosity transitions with hysteretic-like rheology are observed only in controlled shear rate simulations of face-centered cubic (111) layers sheared parallel to the <211> direction with full representation of the hydrodynamic particle interactions. Rheological curves collapse when stresses are scaled by the elastic modulus and shear rates by the elastic modulus divided by the high-shear-rate limiting viscosity. The magnitude of the hysteretic viscosity jump and the scaled critical stresses match experimental values.

Wednesday 3:35 San Carlos I SE10

STRESS RELAXATION IN COLLOIDAL DISPERSIONS

David R. Foss and John F. Brady
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

The stress relaxation behavior of colloidal dispersions is investigated by simulation and theory. For Brownian hard-sphere suspensions, the Brownian contribution to the macroscopic stress is responsible for large low-shear viscosities and shear-thinning behavior; the hydrodynamic contribution varies little with shear rate. The Brownian stress originates from a deformation of the microstructure by the imposed shear flow. The stress autocorrelation function is calculated at equilibrium and measures how the suspension relaxes from microstructural fluctuations. The high-frequency dynamic modulus is related to the zero-time limit of this correlation function and is found to be finite for systems with hydrodynamic interactions and diverge as $t^{-1/2}$ without hydrodynamics. The low-shear viscosity can be determined from the stress autocorrelation function using a Green-Kubo formula and compares well with experiments and previous steady-shear simulations. The relaxation of the stress from non-equilibrium configurations is also examined via shear-cessation simulations.

Wednesday 4:00 San Carlos I SE11

MEASUREMENT OF SHEAR-INDUCED SELF-DIFFUSION IN CONCENTRATED SUSPENSIONS BY A NOVEL METHOD

Dirk Van den Ende, Victor Breedveld, Rob J J. Jongschaap, and Jorrit Mellema
Rheology Group, Dept of Applied Physics, University of Twente, Enschede 7500 AE, Netherlands

Diffusive migration of particles in flowing suspensions is historically associated with Brownian motion of colloids due to interactions with solvent molecules or with inertial effects in case of turbulence. It has been shown experimentally however, that another mechanism exists: large, non-colloidal (about 0.1 mm) particles show diffusion-like behaviour even in low Reynolds numbers flow, where inertia is unimportant. This shear-induced or hydrodynamic diffusion is caused by particle interactions and is a very important phenomenon for understanding the behaviour and structure of flowing suspensions. A new technique has been developed to measure the shear-induced self-diffusivity in a concentrated suspension (20% - 50% solids volume fraction) of non-colloidal spheres (.09 mm average diameter). The method is based on the correlation between the positions of tracer particles in successive images and can be used to determine the self-diffusivity in non-colloidal suspensions on different time-scales. This technique has been tested in the laboratory of A. Acrivos in collaboration with A. Tripathi. The self-diffusivities were measured in the velocity gradient and vorticity direction in a narrow gap Couette device for values of the strain $S \Delta t$ ranging from 0.05 to 0.6, where S is the applied shear rate and Δt is the correlation time. Both diffusivities were found to scale linearly with $S \Delta t$ over the range 0.05-0.6 and are in good agreement with the results of previous studies, although the previous experiments were performed at much larger values of $S \Delta t$. The self-diffusivity in the velocity gradient direction was found to be about 1.8 times larger than in the vorticity direction.

Wednesday 4:25 San Carlos I SE12

FRICTION FORCE MEASUREMENTS ON CELLULOSE SURFACES USING COLLOIDAL PROBE MICROSCOPY

Stefan Zauscher and Daniel J. Klingenberg
Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706

The rheology of concentrated paper pulp and other fiber suspensions is controlled by the forces acting at the contact points between the fibers. These forces, and thus the suspension rheology, can be dramatically altered by the addition of adsorbing polymers. We have measured the normal and tangential forces between model surfaces in water using colloidal probe microscopy. Water soluble polymers affect both the normal and tangential forces at very small addition levels (< 100 ppm). Adsorbed polymers alter the steric interactions between surfaces in a manner that resembles polymer brush interactions. The adsorbed polymer also dramatically decreases the coefficient of sliding friction between the surfaces. We will describe the character of both the normal and tangential forces, and interpret these results in light of the current understanding of interactions between molecularly smooth and rough surfaces.

Wednesday 4:50 San Carlos I SE13

COLLOID GROWTH MODEL FOR VISCOELASTIC GELS

T. S. Chow
Wilson Center for Research and Technology, Xerox Corporation, Webster, NY 14580

The fundamental relationships between the static and dynamic scaling for viscoelastic gels are derived on the basis of a colloid growth model. The scaling of the total number of monomers and the radius of gyration is defined by a static fractal dimension. We have discovered a universal constant,which relates the shear modulus of a polymer gel melt to the glassy shear modulus near the glass transition. The dynamic scaling of the shear relaxation modulus is then obtained as a function of the universal constant and fractal dimension. Analyzing the size-dependent shear viscosity, we have determined the universal constant to be 2.647 in the case of the diffusion-limited aggregation. This new theory not only provides the quantitative predictions of the measured viscosity and viscoelastic exponents at the gel point, but also describes the viscoelastic relaxation of crosslinked polymers far from the sol-gel transition. The theoretical prediction is in good agreement with viscoelastic measurements.

Symposium CF
Coupling Flow and Order in Fluids

Organizer: Lynn Walker

Wednesday 1:30 San Carlos III CF14

VISUALIZATION OF FLOW-INDUCED ORDER AND DYNAMICS BY NMR

Paul T. Callaghan, Melanie M. Britton, and Maria L. Kilfoil
Institute of Fundamental Sciences-Physics, Massey University, Palmerston North, New Zealand

Nuclear Magnetic Resonance Microscopy may be used to obtain detailed information concerning the velocity distribution of a complex fluid undergoing shear and extension. This has enabled the observation of shear-banding effects in wormlike micellar solutions, in pipe, cylindrical couette and cone-and-plate geometries. Recently we have refined the method to permit the study of velocity fluctuations, at time scales ranging from milliseconds to seconds, chloride/sodium salicylate micelle system is subject to rapid fluctuations (1). These fluctuations are extremely sensitive to solution composition.

NMR spectroscopy can provide an indication of molecular order through terms in the spin Hamiltonian which are bi-linear in the spin operators and which transform under rotation as second rank tensors. Furthermore we can localise this spectroscopy by means of special pulse schemes which select any part of the flow field. We have used such selective schemes, along with proton dipolar and deuterium quadrupolar interactions, to investigate ordering in polymer semi-dilute solutions (PEO/water) and melts (PDMS) under shear and extension using a couette cell and four roll mill respectively. By selectively orienting different principal axes of the flow with respect to the magnetic field, we may investigate the order tensor, for example, finding the orientation of the director associated with uniaxial deformation. In the case of polymer melts, main chain labelling should lead to a sampling of the stress/birefringence tensor. In the case where a separate probe molecule is used, for example a chemically identical oligomer, some surprising results emerge (2).

(1) M.M. Britton and P.T. Callaghan, (submitted) 1998.
(2) P.T. Callaghan, M.L. Kilfoil and E.T. Samulski, (submitted) 1998

Wednesday 1:55 San Carlos III CF15

SHEAR-INDUCED PHASE CHANGES IN BLENDS OF POLY(STYRENE-CO-MALEIC ANHYDRIDE) AND POLY (METHYL METHACRYLATE)

Divya Chopra[1], Dimitris Vlassopoulos[1], and Savvas G. Hatzikiriakos[2]
[1]Institute of Electronic Structure and Laser, F.O.R.T.H., Crete, Greece; [2]Dept. Chemical Engineering, The University of British Columbia, N/A, Vancouver, Canada

The effects of shear flow on the phase behavior of a polymer blend with high glass transition temperature, Tg, constituents and small dynamic asymmetry (Tg contrast) were investigated using shear and capillary rheometry, complemented by differential scanning calorimetry and analysis of the extrudates. This blend is a lower critical solution temperature mixture of a random copolymer of styrene and maleic anhydride, SMA, and poly(methyl methacrylate), PMMA. Both shear-induced mixing, at low and very high shear rates, and shear-induced demixing, at moderate shear rates, were observed. In the former case, extrudes were optically transparent, yielded one Tg and were thermorheologically simple at all temperatures up to the capillary extrusion one; on the other hand, extrudates related to shear-induced demixing were opaque, yielded two Tgs and were thermorheologically complex up to the extrusion temperature. The physical mechanism of the shear-induced structural changes apparently relates to different amount of stored elastic energy in the deformed domains of different glass transition and viscosity. We showed how to detect and isolate the degradation effects, which are predominant in SMA at high temperatures, and result in opaque but not necessarily phase-separated samples. The methodology presented here for the determination of the shear-phase diagram in a flowing polymer blend should be applicable to any industrial mixture, and it is of particular value for assessing the effects of strong shear flow, relevant in processing applications. Finally, the method of solution preparation, i.e., solution-cast versus melt-mixed samples, did not affect the rheologically determined demixing temperatures.

Wednesday 2:20 San Carlos III CF16

SHEAR RHEOLOGY AND MICROSTRUCTURE OF CONCENTRATED SHEAR THICKENING COLLOIDAL DISPERSIONS

Joseph Amante[1], Robert J. Butera[2], and Norman J. Wagner[1]
[1]Chemical Engineering, University of Delaware, Newark, DE 19716; [2]DuPont Automotive, DuPont Marshall Lab, Philadelphia, PA 19146

Concentrated, charge stabilized colloidal dispersions are studied by rheology and small angle neutron scattering (SANS). The rheology and shear-induced microstructure are relevant in a number of technological applications of colloidal dispersions, including coatings, inks, pharmaceuticals, pigments, and ceramics. Here, the low shear viscosity and modulus, shear thinning, and shear thickening are studied as a function of surface charge and particle concentration. A model latex copolymer is dialyzed and studied in this work. Flow-SANS is used to study the full three-dimensional microstructure, as well as characterize the interparticle potential. At high concentrations and particle surface charge, the sample is glassy at rest, strongly shear thins, and then exhibits extreme, ``super-critical' shear thickening. The process is reversible, yet some hysteresis is observed in the thixotropic loop. Although no shear-induced order is observed in either the vorticity-velocity, or vorticity-gradient scattering planes, shear thickening is nonetheless observed for these samples. At lower surface charge density and ionic strengths, these samples show some shear alignment, indicating crystallinity. However, these samples do not shear thicken in the range of stresses probed. Indeed, a sample is devised that shows clear order-disorder in the off-axis scattering without any associated shear thickening, demonstrating that an order-disorder transition is not sufficient to induce shear thickening in concentrated, charged dispersions. Quantitative analysis of the flow SANS spectra are used with micromechanics to deconvolute the rheological data in terms of the colloidal forces responsible for the shear viscosity and normal stresses. These results provide quantitative evidence for the forces responsible for the rheology and the link to the shear-induced microstructure.

Wednesday 2:45 San Carlos III CF17

A SIMPLE MODEL FOR SHEAR-THICKENING

Jacqueline L. Goveas[1] **and Glenn H. Fredrickson**[2]

[1]Materials Research Laboratory, University of California at Santa Barbara, Santa Barbara, CA 93106; [2]Department of Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106

We propose a simple model to describe a shear-thickening system. We consider melt polymer Rouse chains with end-stickers, such that two chains can undergo a chemical reaction to form a chain that is twice as long. The application of shear increases the rate of chemical reaction, effectively increasing the system viscosity. We also study whether this mixture of short and long chains is stable with respect to segregating into an inhomogeneous banded system.

Wednesday 3:35 San Carlos III CF18

COMPARISON OF THE EFFECTS OF DIMETHYL AND DICHLORO BENZOATE COUNTERIONS ON DRAG REDUCING AND RHEOLOGICAL BEHAVIORS AND MICROSTRUCTURES OF A CATIONIC SURFACTANT

Zhiqing Lin[1], **Yi Zheng**[2], **Ishi Talmon**[3], **H.T. Davis**[2], **L.E. Scriven**[2], **and Jacques L. Zakin**[1]

[1]Chemical Engineering Department, The Ohio State University, Columbus, OH 43210; [2]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455; [3]Department of Chemical Engineering, Technion-Israel Institute of technology, Haifa 32000, Israel

The effectiveness of cationic surfactants as drag reducers, their rheological behavior and microstructures depend on the chemical structures of their negatively charged counterions. Thread-like micelles that have been reported as necessary for surfactant drag reduction may be formed. Recently, however, we reported the first drag reducing system with a vesicle-dominated microstructure (5mM Arquad 16-50 (commercial CTAC) with 5mM 5-Cl-salicylate) [1] and also good drag reducing systems with microstructures lacking any thread-like micelles, such as nearly equal amounts of vesicles and spherical micelles (5mM Arquad 16-50 with 10mM 3,4-Cl-benzoate) [2] and vesicle-dominated with open vesicles (5mM Arquad 16-50 with 5mM 3-CH3-salicylate) [3]. These microstructures raise questions about assertions that a network of thread-like micelles is necessary for drag reduction to occur. In this paper drag reduction, rheological properties, and cryo-TEM micrographs are described for Arquad 16-50 with 3,4-CH3-benzoate at concentrations of 5mM/5mM (counterion to surfactant) and 10mM/5mM in order to compare results with those of the above mentioned anions, particularly the 3,4-Cl-benzoate system. Both solutions are good drag reducers. The 10mM/5mM solution shows normal viscoelastic behavior and high vis(ext)/vis(shear) while the 5mM/5mM has unusual rheological properties and vis(ext)/vis(shear) ratios close to that of water. Cryo-TEM images are presented to show the microstructures of the two solutions.

[1] Z. Lin, B. Lu, Y. Zheng, D. Digiulio, Y. Talmon, H.T.Davis, L.E.Scriven and J.L. Zakin, AIChE Annual Meeting, LA., Nov., 1997.
[2] Z. Lin, Y. Zheng, Y. Talmon, H.T. Davis, L.E. Scriven and J.L. Zakin, AIChE Annual Meeting, Miami Beach, Nov., 1998.
[3] Z. Lin, Y. Zheng, Y. Talmon, H.T. Davis, L.E. Scriven and J.L. Zakin, 5th European Rheology Conference, Slovenia, Sept., 1998.

Wednesday 4:00 San Carlos III CF19

COUPLING BETWEEN STRUCTURE AND MACROSCOPIC BEHAVIOR OF FLOW-INDUCED STRUCTURES IN DILUTE SOLUTIONS OF CATIONIC SURFACTANTS EXPOSED TO DIFFERENT TYPES OF FLOW FIELDS

Lynn M. Walker[1], Brian G. Thebaud[1], and Jean-Francois Berret[2]
[1]Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213; [2]Groupe de Dynamique des Phase Condensees, Universite de Montpellier II, Montpellier F-34095, France

Structural transitions have been reported in dilute cationic surfactant solutions exposed to shear. These nonequilibrium structures are large and strongly aligned with the direction of shear. The formation of this structure is commensurate with a sudden increase in both viscosity and viscoelasticity of the fluid. In this work, we are interested in understanding how proposed structures lead to the observed changes in macroscopic rheological properties (viscosity and elasticity). We compare the results of small-angle neutron scattering and birefringence studies on dilute solutions of the cationic surfactant cetyltrimethylammonium tosylate (CTAT) in water while exposed to different types of flow fields. In simple shear (Couette) and nonhomogeneous shear (Poiseuille), direct comparisons are made to mechanical measurements of rheological properties to determine if the assumed flow field is maintained and if elastic instabilities play a role in the reported rheological behavior. We also investigate differences in the nature of the structure in the simple and nonhomogeneous shear cases. In uniaxial elongation (opposed nozzle) flow, birefringence has been used as a structural probe. Results are used to compare the structural changes observed in a strong flow field to that observed in weak flow fields (shear).

Wednesday 4:25 San Carlos III CF20

SHEAR INDUCED STRUCTURES IN MICELLAR SURFACTANT SOLUTIONS (MISS) INVESTIGATED BY DOPPLER ULTRASOUND METHOD

Peter Fischer, Boris Ouriev, and Erich Windhab
ILW, ETH Zuerich, Zuerich 8092, Switzerland

Aqueous micellar solutions exhibit a broad range of different rheological properties like linear Maxwell behavior and rather complex non-linear features. In the non-linear flow regime the solutions exhibit several different flow properties depending on the concentration of both surfactant and counterion. For example, the spurt effect, smooth shear thinning that can be described by the Giesekus model, or several kinds of shear induced structures (SIS) are reported /1-3/. In recent studies we observe flow induced phase transition and flow instabilities (FI) simultaneously.

The investigation of the rheological properties of MiSS presented here (transparent and non-transparent samples can be investigated) is based on the superposition of a pressure difference measuring method with the Doppler ultrasound method. The method uses a high frequency ultrasonic beam which is emitted into the flow field to be investigated. The signal is scattered by tracer particles in the flow and the time delay between emitted and received pulse and the frequency shift is determined. This shift, know as the Doppler shift, is related to the speed and the direction of the moving scatterers. The shape of the obtained velocity profile is used to calculated the volumetric flow and the rheological properties of the sample /4/. The combination of the wall stress data and the velocity profile, obtained at the same time and the same place, provides the viscosity function for viscoelastic surfactant systems with and without shear induced structures.

Wednesday 4:50 San Carlos III CF21

RHEOLOGICAL PROPERTIES OF A DILUTE LYOTROPIC SPONGE PHASE L3

H. F. Mahjoub[1], M. Kleman[1], C. Bourgaux[2], and Jean-Francois Tassin[3]
[1]L.M.C.P., T 16, case 115, Univ Pierre & Marie Curie, Paris 75252, France; [2]L.U.R.E, Batiment 209 D, Centre universitaire, Orsay 91405, France; [3]Chimie et Physique des Materiaux Polymeres, UMR 6515, Universite du Maine, Le Mans 72085, France

The L3 (sponge) phase displays usually a large flow birefringence under gentle shaking. We have investigated this property by flow birefringence, in-situ X-ray scattering, and light microscopy observations in specimens of a dilute surfactant system (CpCl - hexanol - brine) sheared in a Couette cell. In the more dilute L3 phase ($0.05 < \phi_{surfactant} <$

0.17) we observe under shear a remarkable transition to a lamellar phase at low shear (~ 50 s^{-1}), while the less dilute ($0.17 < \phi_{surfactant} < 0.35$) does not transform. Relaxation times show up different scaling laws in the two domains of dilution, pointing towards fundamental differences in the structural properties of these 2 domains of concentrations. The combination of the various techniques allows us to describe the molecular events occuring during the shear induced phase transition. It will be shown, that lamella are first formed with their normals parallel to the vorticity axis of the cell. Than a collective tumbling motion of the lamella is observed which after some shearing time sets the lamella with their normals aligned along the velocity gradient direction. The examination of several concentrations shows that the rate of the tumbling motion is linked to the shear rate.

Symposium SL
Rheology of Solids

Organizers: Andre Lee and Gregory B. McKenna

Wednesday 1:30 San Carlos II SL10

SHAPE MEMORY EFFECT IN INORGANIC-ORGANIC HYBRID POLYMERS

Hong G. Jeon[1], Patrick T. Mather[2], and Timothy S. Haddad[3]
[1]Systran Corp., Air Force Research Lab, Wright Patterson AFB, OH 45433-7750; [2]Materials Directorate, Air Force Research Lab, Wright Patterson AFB, OH 45433-7750; [3]Raytheon STX, Air Force Research Lab, Edwards AFB, CA 93524-7680

The microstructure and shape memory properties of norbornyl-POSS hybrid copolymers having either cyclohexyl corner groups (CyPOSS) or cyclopentyl corner groups (CpPOSS) were investigated by wide-angle x-ray scattering, transmission electron microscopy, and thermomechanical analysis. Here, POSS refers to the polyhedral oligomeric silsesquioxane macromer. Samples containing 50wt% of POSS macromer have been drawn in a tensile mode to various draw ratios at temperatures above their Tgs, followed by rapid quenching in LN2. Our results show that the direction of POSS-POSS correlation is preferentially oriented along the draw axis, while orientation of polynorbornene chains along the draw axis is hindered (relative to pure polynorbornene) due to intermolecular POSS-POSS interactions. Shape memory properties of such drawn samples were also explored by measuring recovered strain while heating above the glass transition temperature using thermomechanical analysis. Our discussion will focus on the shape recovery behavior, such as recovery amplitude, rate, and strength, as affected by microstructural changes depending on the different corner groups in the POSS macromer.

Wednesday 1:55 San Carlos II SL11

STUDY ON THE POLYSTYRENE/HIGH DENSITY POLYETHYLENE BLENDS FROM AN EXTRUSION PROCESS

Bin Xu[1], John Simonsen[2], and W. E. Skip Rochefort[1]
[1]Chemical Engineering Department, Oregon State University, Corvallis, Oregon 97331; [2]Forest Products Research Lab, Oregon State University, Corvallis, Oregon 97331

The mechanical properties, creep resistance, thermal properties and morphology have been determined to high molecular weight Polystyrene/High Density Polyethylene blends made from either a slot die attached to an extruder or compression molded samples. HDPE was the continuous phase even when the PS content was as high as 50%(wt.). At 75%PS-25%HDPE blend, co-continuous phases were observed in the machrine direction. Ribbon-like PS dispersion phase was observed in the 25%PS-75%HDPE and 50%PS-50%HDPE samples from extrusion process. It was found that the modulus of elasticity of these blends could be estimated by the Rule of Mixtures even in the absence of a compatibilizer. There was a strong relationship between mechanical properties and morphology due to processing. For 50%PS-50%HDPE blends, the stress-strain curves from extruded samples had a HDPE-like behavior, while the samples from compression molding gave in a brittle, PS-like curve. The extruded samples possessed 50% higher tensile strength than those from compression molding. This suggested that the ribbon-like, dispersed PS acted as a reinforcing material inside the HDPE matrix. The creep experiments were performed in three-point bending. They showed that 50%PS-50%HDPE and 75%PS-25%HDPE have greater creep resistance

than pure PS. 75%PS-25%HDPE had the highest creep resistance of all blends from extrusion. Mechanical properties and creep resistance were also measeured for PS/HDPE/Wood flour composites. The creep resistance increased with increasing wood flour content.

Wednesday 2:20 San Carlos II SL12

PRESSURE WAVE STABILITY IN GRANULAR FLOW

T Astrita[1], Raffaella Ocone[2], and A. Pascarelli[3]

[1]Energetic, Thermofluodynamics and Environmental Control, University di Napoli A Federico, Naples, Italy; [2]Chemical, Environmental and Mining Engineering, University of Nottingham, Nottingham, United Kingdom; [3]Mechanical Engineering, University of Maryland, College Park, MD

In this work, following an analogous route developed in gas dynamics, and using thermodynamic tools developed by Ocone and Astarita, we approach the problem of pressure wave stability. As gases, granular materials are intrinsically compressible. Although the intrinsic particle density is constant, the solid volume fraction, hence the local averaged density of the particulate phase, may well change in space and time. In classical gas dynamics the difference between an incompressible and a compressible flow may be easily defined and quantitatively verified introducing the concept of steady and isentropic flow. In this way, it is possible to reduce the independent thermodynamic variables to only one. Furthermore, after having defined the Mach number, M, as the ratio of the local velocity and the speed of sound in the same point, it is possible to consider the ratio of the static and stagnation values of each thermodynamic variable which is a function only of the Mach number. In particular, from the value of the density ratio it is possible to have an insight of "how" compressible the flow is. Since the density ratio is a monotonically decreasing function of the Mach number, by fixing the accuracy, it is possible to find a M such that the flow can be assumed incompressible. In granular flow the situation is more complex; even if a theory of granular thermodynamics has been recently developed. Due to the inelasticity of particle-particle and/or particle-wall collisions, there is always a dissipation of internal pseudoenergy and hence a change of the entropy level. A way to overcome this problem is to assume that there is a positive influx of energy from the walls, considering, for instance, vibrating walls. Since we mostly wish to discuss the logical status of the unsteady compressible granular flow, we use what is probably the simplest possible example of the problem: a basic flow that it is maintained in a thermalised state by vibration of a constant section conduit.

Wednesday 2:45 San Carlos II SL13

VISCOELASTIC PROPERTIES OF CARBON FIBER REINFORCED POLYSULFONE COMPOSITE AS A NEW BIOMATERIAL

Kang Sun[1], Chang Chun Chen[2], Ren Jie Wu[1], Chee Yoon Yue[3], and Min Wang[3]

[1]Institute of Composite Materials, Shanghai Jiaotong University, Shanghai 200030, China; [2]School of Materials Science & Engineering, Shanghai Jiaotong University, Shanghai 200030, China; [3]School of Mechanical & Production Engineering, Nanyang Technological University, Singpaore 639798, Singapore

Polysulfone (PSF) due to its good biocompatible properties, has been reinforced with carbon fibers to produce an implant material which would closely match the mechanical properties of human bone. According to results obtained from finite element analysis of hip prosthesis, the unidirectional composites was made, which contains 28.9 volume percent of carbon fiber as the reinforcement. Both the raw materials and the composite were characterized using various techniques. It was determined that the composite had a density of 1.34 gm/c.c., and its tensile strength and modulus were 458.5 GPa and 46.9 GPa, respectively, which are considerable lower than those of surgical grade Ti alloy. Viscoelastic properties of the composite were also investigated using two testing systems to measure both storage and loss moduli (either longtiudinally and transversely). When tested longitudinally, it was found that the storage modulus drop form 9 GPa to 0.4 GPA around 180C. When tested transversely, with increasing temperature, the storage modulus decreased faster in the low frequency range than in the high frequency range, while the loss modulus has a reverse trend. As the temperature approach 180C, the loss modulus became equal to the storage modulus. It is shown that the overall viscoelastic properties of PSF composite followed the same tendency as other PMC. These results clearly identified that rheological measurements and dynamical mechanical analysis are useful in understanding the viscoelastic behavior of this composite, which can contribute to further improvement of the material for medical applications.

Symposium EM
Rheology and Microstructure of Electro and Magneto-Rheological Fluids

Organizer: Jon Bender

Wednesday 3:35 San Carlos II EM1

MAGNETORHEOLOGY WITH NON-NEWTONIAN SUSPENDING MEDIA

Peter J. Rankin and Daniel J. Klingenberg
Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706

The rheological properties of magnetorheological (MR) fluids, which consist of magnetizable particles in nonmagnetizable liquids, are altered by applied magnetic fields transverse to the direction of flow. The apparent viscosities of MR fluids can increase by several orders of magnitude by applying magnetic field intensities on the order of 0.1 kA/mm. Traditionally MR fluids have been made with Newtonian suspending media, where sedimentation is often a problem. In an effort to reduce the effects of sedimentation, we employed non-Newtonian continuous phases in MR fluids. We will report on the influence of continuous phases with a yield stress on the steady-state rheology, dynamic rheology, and structure formation in MR suspensions. Preliminary results indicate that non-Newtonian continuous phases can prevent sedimentation in MR suspensions. Furthermore, it appears that the field-induced yield stress of MR fluids changes very little when switching from Newtonian to non-Newtonian continuous phases, provided that the field strength is high enough. At lower field strengths, MR suspensions made with non-Newtonian continuous phases have smaller yield stresses than MR suspensions made with Newtonian continuous phases. We also found that in steady-shear experiments of MR fluids made with non-Newtonian continuous phases, the time it takes the shear stress to reach its steady-state value is largely independent of the applied magnetic field strength.

Wednesday 4:00 San Carlos II EM2

MAGNETORHEOLOGICAL AND SUSCEPTIBILITY PROBES OF MAGNETIC PAINTS

Andrei Potanin[1], Ronald J. Hirko[2], Viktor T. Peikov[3], and Alan M. Lane[4]
[1]Rheology, Quantegy, Inc., Opelika, Al 36803-0190; [2]Chemical Lab., Quantegy, Inc., Opelika, Al 36803-0190; [3]Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, Al 35487; [4]Chemical Engineering, The University of Alabama, Tuscaloosa, Al 35487-0203

Linear viscoelastic measurements with and without a superimposed magnetic field are used to characterize the structure of model magnetic paints comprised of metal particles, cyclohexanone and polyvinylchloride wetting resin. The storage modulus, G', rapidly increases above certain magnetic field, Hcrit, which characterizes dispersion quality by how easily particles align under the field. Milling weakens the structure of the paint, provided sufficient resin concentration is maintained, as revealed by a decrease of G' and Hcrit with milling time. Magnetorheological measurements are correlated with susceptibility measurements in a small alternating magnetic field with frequency from 10 Hz up to 10 KHz, which probes particle interactions without breaking the structure. Relaxation time spectra were extracted from the complex susceptibility and compared to rheological spectra extracted from linear viscoelastic measurements. The methods compliment each other over eight orders of magnitude of relaxation time. Rheological spectra shift to shorter relaxation times as resin concentration increases, since structure is transformed from a large-scale network to smaller scale aggregates. Susceptibility spectra shift to longer times as resin concentration increases, which is attributed to weakening of particle interactions.

Wednesday 4:25 San Carlos II EM3

MODELING AND COMPUTATION OF THE EFFECTIVE MAGNETIC PROPERTIES OF MAGNETORHEOLOGICAL FLUIDS

Tammy M. Simon[1], H. T. Banks[1], Kazufumi Ito[1], Mark R. Jolly[2], Beth C. Munoz[3], and Fernando Reitich[4]
[1]Center for Research in Scientific Computation, North Carolina State University, Raleigh, NC 27695; [2]Advanced Technologies Research Group, Lord Corporation, Cary, NC 27511-7900; [3]Cyrano Sciences, Inc., Pasadena, CA 91107; [4]School of Mathematics, University of Minnesota, Minneapolis, MN 55455

It is well known that the rheological behavior of magnetorheological (MR) fluids can be controlled with a changing magnetic field. Understanding the magnetic properties of MR fluids is important to the design of MR fluid-based devices and also provides valuable insight into the character of the microstructure responsible for the field-responsiveness. However, computing the magnetic properties is difficult due to the highly oscillatory nature of the magnetization of the individual constituents. In fact, a direct calculation of the magnetic response entails the solution of elliptic differential equations for the magnetic scalar potential with rapidly oscillating permeabilities. Thus, numerical methods based on standard finite elements become prohibitively expensive. Hence, in this presentation, we investigate modeling the effective magnetic properties of MR composites by appealing to the mathematical theory of homogenization. We consider fluids which present periodic microgeometries of spherical chains and study the linear and nonlinear constitutive laws of the composites. Finally, we compare our numerical results with experimental data and with some other approximations and bounds (e.g. Maxwell, Rayleigh-Lam, Hashin-Shtrikman) found in the literature.

Wednesday 4:50 San Carlos II EM4

DYNAMICS SIMULATIONS AND EFFECTIVE PROPERTIES FOR MAGNETO-RHEOLOGICAL FLUIDS

Hung V. Ly[1], H. T. Banks[1], Kazufumi Ito[1], Mark R. Jolly[2], and Fernando Reitich[3]
[1]Center for Research in Scientific Computation, North Carolina State University, Raleigh, NC 27695-8205; [2]Advanced Technologies Research Group, Lord Corporation, Cary, NC 27511-7900; [3]School of Mathematics, University of Minnesota, Minneapolis, MN 55455

We have developed a numerical code that involved the fast multipole method to determine the magnetostatic potentials and fields of the inhomogeneous magnetorheological fluids with large number of inclusion particles in a nonconducting medium when subject to an applied magnetic field at the boundary. Its speed and accuracy allow us to study numerically many important physical phenomena at the microstructural level in MR fluids. Of particular interest are the dynamic simulations. Here this code quickly provides us the magnetostatic force calculated from the Maxwell stress tensor for every single particle. By combining the magnetostatic force with the hydrodynamic and repelling forces, we can determine the motion of each particle as it evolves in time. In this presentation, we first focus on the response for structure formation from the dynamic simulations and the dependency of structure formation on fluid parameters such as carrier viscosity, volume fraction and the intensity of the applied magnetic field, etc. We also elaborate on parametric studies of the effective dynamic properties on MR fluids. Related experimental results will be discussed in the context of our efforts.

Symposium AN
Analytical and Numerical Solutions to Flow Problems

Organizer: Michael Renardy

Wednesday 1:30 Los Angeles AN6

STRUCTURE OF THE SPECTRUM IN ZERO REYNOLDS NUMBER SHEAR FLOW OF THE UCM AND OLDROYD-B LIQUIDS

Helen J. Wilson[1], Michael Renardy[2], and Yuriko Renardy[2]

[1]DAMTP, University of Cambridge, Cambridge CB3 9EW, United Kingdom; [2]Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

We provide a mathematical analysis of the spectrum of the linear stability problem for one and two layer channel flows of the upper-convected Maxwell (UCM) and Oldroyd-B fluids at zero Reynolds number. For plane Couette flow of the UCM fluid, it has long been known that, for any given streamwise wave number, there are two eigenvalues in addition to the continuous spectrum. In the presence of an interface, there are seven discrete eigenvalues. In this paper, we investigate how this structure of the spectrum changes when the flow is changed to include a Poiseuille component, and as the model is changed from the UCM to the more general Oldroyd-B. For a single-layer UCM fluid, we find that the number of discrete eigenvalues changes from two in Couette flow to six in Poiseuille flow. The six modes are given in closed form in the long wave limit. For plane Couette flow of the Oldroyd-B fluid, we solve the differential equations in closed form. There is an additional continuous spectrum and a family of discrete modes. The number of these discrete modes increases indefinitely as the retardation time approaches zero. We analyze the behavior of the eigenvalues in this limit.

Wednesday 1:55 Los Angeles AN7

INSTABILITY DUE TO SECOND NORMAL STRESS STRATIFICATION IN TWO-LAYER CHANNEL FLOW OF THE GIESEKUS FLUID

Yuriko Renardy and Michael Renardy

Mathematics, Virginia Tech, Blacksburg, VA 24061-0123

The two-layer Couette flow of superposed Giesekus liquids is examined. In order to emphasize the effect of a jump in the second normal stress difference, the analysis is focused on flows where the shear rate and first normal stress difference are continuous across the interface. In this case, the flow is neutrally stable to streamwise disturbances, but can be unstable for spanwise disturbances driven by a jump in the second normal stress difference. The mode of maximum growth rate gives rise to stationary ripples perpendicular to the flow. The eigenvalue problem for purely spanwise wave vectors can in principle be solved analytically.

Wednesday 2:20 Los Angeles AN8

STUDIES ON FIBER SPINNING - SOLVABILITY AND SPECTRAL ANALYSIS IN THE NONISOTHERMAL VISCOUS CASE

Thomas Hagen and Michael Renardy

Department of Mathematics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0123

We shall discuss the equations of fiber spinning in nonisothermal unsteady viscous flow. These nonlinear equations model the uniaxial extension of a viscous fluid thread, based on the thin filament approximation.

Our discussion will address the following topics: First we shall prove existence, uniqueness and regularity of solutions. These results are achieved by a fixed-point argument, applied to a sequence of approximating solutions. Next we will give a rigorous proof that the stability of solutions for the linearized equations is entirely determined by the eigenvalues of the corresponding differential operator. Finally, by using a spectral collocation method, we shall derive some numerical results on the eigenvalue distribution.

Wednesday 2:45 Los Angeles AN9

THE EFFECT OF NON-ZERO SECOND NORMAL STRESS DIFFERENCE ON FLOW IN CURVED PIPES

Anne M. Robertson[1], **Witasanachai Jitchote**[2], **and Supalerk Chanchawichak**[3]

[1]Department of Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA 15261; [2]Royal Thai Army, Thanyaburi, Phathumthani 12130, Thailand; [3]Department of Mechanical Engineering, University of Pittsburgh, Pittsburgh, PA 15261

Perturbation methods have been used to obtain analytical solutions for steady flow of viscoelastic fluids in curved pipes of circular cross section where the perturbation parameter is the radius of the pipe cross section divided by the radius of curvature of the pipe. Previously, viscoelastic fluids with *zero second normal stress difference* have been studied, and the secondary motion for both creeping and non-creeping flows has been shown to be qualitatively similar to that arising from centrifugal effects in Newtonian fluids. Namely, in addition to the primary flow, there is a secondary motion consisting of a pair of counter-rotating vortices (see, e.g. Bowen, Davies, Walters, JNNFM,**38**,1991 and Robertson and Muller, Int. J. Non-Linear Mechanics,**31**,1996). In this work, we have obtained perturbation solutions for two constitutive equations with *non-zero second normal stress difference*: the classical second order fluid and the modified Oldroyd-B fluid introduced by Shaqfeh, Muller and Larson (JFM,**235**,1992). We find cases in which the secondary motion of fluids with non-zero second normal stress difference is qualitatively different than that arising in fluids with zero second normal stress difference.

Wednesday 3:35 Los Angeles AN10

INVESTIGATION OF THE INFLUENCE OF RHEOLOGICAL PARAMETERS ON DRAG REDUCTION, REYNOLDS STRESS AND VORTICITY BUDGETS THROUGH DIRECT NUMERICAL SIMULATIONS.

Costas D. Dimitropoulos[1], **R. Sureshkumar**[2], **and Antony N. Beris**[1]

[1]Chemical Engineering, University of Delaware, Newark, DE 19716; [2]Chemical Engineering, Washington University, St. Louis, MO

This work continues our attempts to elucidate theoretically the mechanism of the turbulent drag reduction phenomenon through direct numerical simulations. As before, we consider a fully turbulent viscoelastic channel flow, using an independently evaluated rheological model for the polymer stress.

In this work, we have identified the proper scaling of quantities representing important structural information for the turbulent flow-field in the case of viscolelastic fluids. As a result, we have seen that there is great consistency in the results for different combinations of the polymer concentration and chain extension, which helps us demonstrate that our obervations are applicable to very dilute systems, not possible to simulate with the current supercomputers. As in our previous work, the simulation results are consistent with the hypothesis that one of the prerequisites for the phenomenon of drag reduction is sufficiently enhanced extensional viscosity, corresponding to the level of intensity and duration of extensional rates typically encountered during the turbulent flow, as has been proposed by various investigators in the past.

Finally, we compare results for the budgets of the Reynolds stress and the vorticity production for different magnitudes of the extensional viscosity of the fluid. Based on these results we discuss the importance of relaxation effects on turbulence modeling for viscoelastic systems.

Wednesday 4:00 Los Angeles AN11

A MODEL OF TURBULENT DRAG REDUCTION FOR DILUTE POLYMER SOLUTIONS

Valentine A. Gorodtsov[1] **and Arkady I. Leonov**[2]

[1]Fluid Mechanics Laboratory, Institute of Problems in Mechanics, Moscow 117526, Russia; [2]Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

A model of pulsating sub-layer in near-wall turbulence (NWT) known for viscous liquids, is extended to describe the drag reduction phenomena in dilute polymer solutions. The model mimics quasi-periodic "bursts" of near wall

eddies and treat them as a non-steady stochastic shearing process in a viscoelastic liquid, with the Poisson distribution of burst instants. The Oldroyd B constitutive equation (CE) whose parameters are evaluated by the Rouse model, is employed to describe the viscoelasticity in dilute polymer solutions. The mean characteristics of the NWT model in the viscoelastic liquid are then found using averaging over the Poisson distribution. The averaged characteristics of the sub-layer are then matched with those known for the developed turbulence. No fitting parameters are involved in these matching conditions. The calculations of the flow in a circular pipe showed that as compared with a viscous liquid, the viscoelastic model predicts drag reduction, increase in the mean period between the bursts, as well as the increase in thickness of the sub-layers. In the realistic case of small polymer additives, the model demonstrates the "Virk asymptote" on the plot of drag coefficient l versus Reynolds number Re. The maximum of drag reduction effect usually happens at very high Re. The calculations of pulsations also made in tghe work, demonstrated that in comparison with viscous liquids, the viscoelastic NWT model predicts a decrease in the transversal pulsations and an increase in longitudinal pulsations with shifting their maximum away from the wall Finally, it is shown that the effect of turbulent drag reduction is accompanied by the reduction in transfer processes of neutral additives (e.g. temperature). All the above theoretical predictions are in good qualitative agreement with known experimental data.

Wednesday 4:25 Los Angeles AN12

GALERKIN AND LEAST SQUARE FINITE ELEMENT APPROACH FOR VISCOELASTIC FLUID FLOWS

Achuth Rao and J. N. Reddy
Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843

A de-coupled finite element analysis for flow of viscoelastic fluid is presented based on the lines of work by Luo and Tanner (1). The solution of the flow equations is separated from that of the constitutive equations. The viscoelastic constitutive equations used for the analysis are expressed in terms of an internal structural parameter, the conformation tensor. These constitutive equations are derived using the Poisson bracket approach as in Beris and Edwards (2), by expressing the Hamiltonian and the dissipation of the flowing system as a functional involving the velocity vector and structural parameter(s). The White Metzner constitutive equation expressed in this form is considered. The equations are solved using the Galerkin (penalty) finite element formulation for the conservation of momentum and least square finite element model for the constitutive equations. Results are presented for flow in a converging channel and extrudate swell from a two-dimensional die.

(1) Luo, X. L. and Tanner, R. I., J. Non-Newtonian Fluid Mech., 31, 143-162, 1989
(2) Beris, A. N. and Edwards, B. J, Thermodynamics of flowing systems with internal microstructure, Oxford University press, Oxford, 1994.

Wednesday 4:50 Los Angeles AN13

A NEW METHOD TO COMPUTE A VISCOELASTIC FLOW PROBLEM USING INTEGRAL CONSTITUTIVE EQUATIONS

E.A.J.F. (Frank) Peters, Martien A. Hulsen, and Ben H.A.A. van den Brule
Mechanical Engineering and Marine Technology, Delft University of Technology, Delft 2628 AL, Netherlands

Integral constitutive equations are notoriously difficult to use in a complex flow problem. In an Eulerian approach one has to integrate back along the streamlines, which is a formidable task in a time dependent problem. This problem is removed in a Lagrangian implementation but then one is confronted with a distortion of the mesh which forces a regular remeshing of the problem.

Both these shortcomings are removed in the new method we propose here. The key idea is to store the deformation history of the problem in so-called configuration fields. A configuration field typically starts its life as a unit tensor field and is then deformed affinely by the flow field. This way of convecting configurational information can be done in an Eulerian way without the need for particle tracking or a Lagrangian method. With the ageing of the field its weight in the final expression for the stress tensor decreases until its contribution to the total becomes negligible.

To verify the code we used the falling sphere benchmark problem. First we used the integral formulation of the Upper Convected Maxwell model and compared the results with the many references that are reported in the literature. Next, we performed a simulation with the Papanastasiou, Scriven, Macosko equation and compared against the results obtained by Rasmussen and Hassager.

Thursday Morning

Symposium SE
Suspensions and Emulsions

Organizers: Norman J. Wagner and Robert J. Butera

Thursday 8:05 San Carlos I SE14

RHEOLOGICAL CHARACTERIZATION OF THE LIQUID-SOLID TRANSITION IN COLLOIDAL GELS -- LESSONS FROM POLYMERS

Robert J. Butera
DuPont Automotive, DuPont Marshall Lab, Philadelphia, PA 19146

It is well established that chemically and physically crosslinking polymer systems at the gel point show a distinct power law relaxation behavior in the oscillatory shear frequency spectrum. We have found that colloidal systems also can pass through a power law relaxation regime that is phenomenologically similar to that of polymers at the gel point, suggesting that this signature may be indicative of the colloidal gel point. Although we do not believe that this behavior is universal for all colloidal gels, we have observed this type of power law relaxation in a wide variety of colloidal systems. Results from several of these systems will be presented and, although it is not yet possible to extract quantitative structural parameters from this data, the implications for use of these measurements as a means to elucidate the microstructure of flocculated colloidal suspensions will be discussed.

Thursday 8:30 San Carlos I SE15

EFFECT OF OSCILLATORY PRE-SHEAR ON THE ELASTIC MODULUS OF COLLOIDAL GELS: MICROSTRUCTURAL INTERPRETATION USING FRACTAL CONCEPTS

Srinivasa R. Raghavan[1], Andrei Potanin[2], and Saad A. Khan[1]
[1]Dept. of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7905;
[2]Rheology, Quantegy, Inc., Opelika, Al 36803-0190

Colloidal gels formed by interacting particles in liquid media consist of a volume-filling network of fractal clusters. An important issue of interest is to obtain scaling relations for the elastic modulus (G') as a function of particle volume fraction ϕ, i.e. $G' \sim \phi^n$. A wide range of values for the exponent n have been experimentally found, contrary to theoretical predictions which point to a small range of allowable values for n. This can be attributed not only to the complex, heterogenous structures existing in these systems, but also to the fact that n depends on the type and extent of **pre-shear** applied on the sample.

In an earlier study (J. Rheol. 39, 1311, 1995) we investigated the effects of large-amplitude oscillatory pre-shear on fumed-silica gels. Following pre-shear, we studied the rebuilding of network structure by monitoring the elastic modulus (G') as a function of time. Quite surprisingly, we found that moderate strains (~ 30%) degraded the gel significantly, whereas large-amplitude (~ 1000%) oscillations restored the gel to near-equilibrium state. In a continuation of the earlier work, we investigate how the $G' - \phi$ relationship is altered on account of oscillatory pre-shear. These results are then interpreted using a microrheological model which can implicitly account for shear-induced changes in fractal networks. We will thus show that moderate oscillatory shear induces an *increase* in the network fractal dimension. We will also present additional rheological experiments, involving complex strain histories, which provide further evidence for our arguments.

Thursday 8:55 San Carlos I SE16

PARTICLE MOTION IN NEWTONIAN AND VISCOELASTIC FLUIDS: SIMULATION AND EXPERIMENT

Housam Binous, Ronald J. Phillips, Scott Porter, and Serge Bobroff
Dept. of Chemical Engineering and Materials Science, University of California - Davis, Davis, California 95616

We have performed experiments and simulations of the motion of two, three and six spheres sedimenting in Newtonian and non-Newtonian fluids. The interesting qualitative differences between our experimental results in fluids with varied rheological characteristics will be presented, and they will be compared with the predictions of our numerical simulations under varying degrees of approximation. We have also performed simulations of non-spherical particles and groups of spheres suspended in steady and oscillatory shear flows over a range of shear rates. The effects of elasticity in the fluid on particle orientation and chaining will be presented and compared with experimental and theoretical results from the literature.

Thursday 9:20 San Carlos I SE17

RELATIONSHIP BETWEEN THE STEADY STATE AND THE COMPLEX OSCILLATORY SHEAR VISCOSITY IN PLANAR RANDOMLY ORIENTED CONCENTRATED FIBER SUSPENSIONS

Colin J. Servais and Jan-Anders E. Månson
Laboratoire de Technologie des Composites et Polymères, Ecole Polytechnique Federale de Lausanne, Lausanne CH-1015, Switzerland

An analytical model for in-plane randomly oriented concentrated fiber suspensions in molten polypropylene has been combined with the Rutgers-Delaware model for Herschel-Bulkley materials. In this new model, it was assumed that at high fiber volume fractions the main contribution to the bulk stress was due to fiber-fiber interactions at the contact points between fibers. Coulombic friction and hydrodynamic lubrication were shown to be the dominant interaction mechanisms. Friction forces dominated at low relative velocities between the fibers whereas lubrication forces dominated at high velocities; this suggests that these forces apply sequentially, generating both solid-like and liquid-like stresses in the suspensions.

The complex viscosity and the steady state viscosity of the suspensions were measured as a function of effective strain rate, which was defined as the strain rate in steady state shear and the product of the strain and the frequency in oscillatory shear. Two types of fiber reinforcements were investigated, namely dispersed fiber and fiber bundle mats. Despite their structural differences, both systems validated the assumptions made. Four distinct materials strain regions were identified: viscoelastic behavior below an apparent yield stress, solid-like behavior at low effective shear rates above the yield stress, a viscous Newtonian plateau at medium effective shear rates, and a shear thinning region at high rates, the two last regions were modeled from the viscosity curves of the neat resins. The model, incorporating parameters obtained by independent experiments, correlated well with the measured shear viscosity. Combined with other models, this work may be used in flow simulation and for the development of new combinations of fiber reinforcements and suspending fluids.

Thursday 10:10 San Carlos I SE18

MEASUREMENTS OF STRUCTURE AND RHEOLOGY OF FIBER SUSPENSIONS IN NEWTONIAN AND VISCOELASTIC FLUIDS

Michael P. Petrich, Claude Cohen, and Donald L. Koch
School of Chemical Engineering, Cornell University, Ithaca, New York 14853

The shear viscosity of a fiber suspension is highly dependent on its microstructure. As a result, considerable insight can be gained from experiments that measure the orientation distribution and rheology of the same fiber suspensions. We have developed highly viscous, index-of-refraction-matched suspensions suitable for such studies. The orientation distribution and rheology of the suspensions are measured in cylindrical Couette flows.

Our Newtonian fluid is a mixture of two viscous polybutenes and a high index of refraction plasticizer. Our measurements in semi-dilute, glass fiber suspensions corroborate existing theories that determine the rheology based

on purely hydrodynamic fiber interactions and assume that the fibers are non-Brownian and are distributed among the Jeffery orbits by hydrodynamic rotary diffusion. At higher concentrations, we observe an abrupt increase in the shear viscosity. The orientation measurements will help us to explain the physical origin of this increase.

A Boger fluid is used to evaluate the effects of elasticity. This viscoelastic fluid with a shear-rate-independent viscosity has been prepared by adding a high molecular weight polystyrene to a solution of low molecular weight polystyrene in dimethyl phthalate. In this case, the microstructure of the fiber suspension is determined by the competing effects of fiber-fiber interactions and the polymer stress. Similar measurements in this system will further enhance our understanding of the relationship between fiber orientation distribution and suspension viscosity.

Thursday 10:35 San Carlos I SE19

DYNAMICS OF NONUNIFORM FIBERS

Paal Skjetne[1], Christian F. Schmid[2], and Daniel J. Klingenberg[2]
[1]Department of Chemical Engineering, SINTEF Applied Chemistry, Trondheim N-7034, Norway; [2]Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706

The dynamics of rigid, axisymmetric bodies are well-established, as described by Jeffery's analysis [G. B. Jeffery, Proc. R. Soc. London, Ser. A 102, 161 (1922)]. However, the behavior of nonuniform fibers (nonaxisymmetric or flexible fibers) can deviate significantly from Jeffery's predictions. For example, flexible fiber orbits drift [P. Skjetne and D. J. Klingenberg, J. Chem. Phys., 107, 2108 (1997)], and triaxial ellipsoids can undergo chaotic dynamics [A. L. Yarin, O. Gottlieb, and I. V. Roisman, J. Fluid Mech., 340, 83 (1997)]. In this presentation, we will describe the dynamics of nonuniform fibers---rigid, nonaxisymmetric fibers, as well as flexible fibers with and without permanent nonaxisymmetric deformations---and how these dynamics differ from those of rigid axisymmetric bodies. Using stability analyses and simulations wherein a fiber is modeled as a chain of osculating rigid bodies, we will provide insight into the mechanisms governing the complex dynamics of these systems. We will also present results illustrating the behavior of concentrated suspensions of nonuniform fibers, and how they differ from suspensions of uniform fibers.

Thursday 11:00 San Carlos I SE20

NMR IMAGING OF BATCH FLOTATION AND SEDIMENTATION

Stephen A. Altobelli[1], Joseph D. Seymour[1], and Lisa A. Mondy[2]
[1]New Mexico Resonance, Albuquerque, NM 87108; [2]Fluids Engineering, Sandia National Laboratories, Albuquerque, NM

Batch sedimentation and flotation are widely used and studied processes. The impetus for these particular studies was an IC manufacturing issue. Concentrated, non-colloidal, non-neutrally buoyant suspensions slowly separating due to gravity were studied by Nuclear Magnetic Resonance Imaging techniques. Previous NMR studies focussed on nearly mono-disperse suspensions and the effects of hydrodynamic dispersion and small polydispersivity on front spreading. The solid phase of interest here is, however, very polydisperse with a substantial fraction of fines, and so techniques which depend on observing a clearing front are not useful. We developed a new method for determining the average vertical velocity of the liquid and solid phases throughout the flotation process. This allows one to measure the hindered settling function in a single experiment. The technique was also applied to slightly polydisperse suspensions. Extensions of this work involving NMR measurement of higher order motional parameters will also be discussed.

*This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Thursday 11:25 San Carlos I SE21

HYDRODYNAMIC PARTICLE MIGRATION: A CONTINUUM LIMIT

Wendy L. Fisher[1], Alan L. Graham[1], James R. Abbott[2], Lisa A. Mondy[3], and Stephen A. Altobelli[4]

[1]ESA-WMM, Los Alamos National Laboratory, Los Alamos, NM 87545; [2]ESA-EPE, Los Alamos National Laboratory, Los Alamos, NM 87545; [3]Fluids Engineering, Sandia National Laboratories, Albuquerque, NM; [4]New Mexico Resonance, Albuquerque, NM 87108

Initially well-mixed suspensions of large spherical particles in viscous Newtonian fluids subjected to continuous nonhomogeneous shear flows demix and establish large concentration gradients. Experiments have been performed in a wide-gap Couette, where the particles were found to migrate from the higher shear-rate regions near the rotating inner cylinder to the lower shear-rate regions near the stationary outer wall. However when using various particle sizes, the time scale observed for the experiments did not match the model predictions. The purpose of this study is to examine the effect of particle size and concentration on the migration rate. To quantify the particles size, the number of particle diameters to the Couette gap ($\Delta R/2a$) while be used. Results indicate that for $\Delta R/2a > 50$, the rate depends on particle size squared as has been predicted by several models. For $\Delta R/2a < 50$, a correction factor needs to be applied which varies from about 0.5 to 5 with a value of 1 at $\Delta R/2a = 50$.

Acknowledgments: This work was supported by the United States Department of Energy under Contract W-7405-ENG-36 at Los Alamos National Laboratory and under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy. The authors gratefully acknowledge partial support for this work through the U.S. Department of Energy, Division of Engineering and Geosciences, Office of Basic Energy Sciences.

Thursday 11:50 San Carlos I SE22

SHEAR-INDUCED PARTICLE MIGRATION IN CONCENTRATED SUSPENSIONS OF NONCOLLOIDAL PARTICLES

Melquiades Allende and Dilhan M. Kalyon

Department of Chemical Sciences & Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030

Migration of rigid particles in non-homogeneous shear flows, driven by shear rate and concentrations gradients, in the transverse to flow direction and in the absence of inertial effects is well documented by Acrivos and coworkers (Gadala-Maria and Acrivos, and Leighton and Acrivos). Use of NMRI and laser-Doppler techniques have provided further wherewithal to elucidate migration effects in Couette and Poiseuille flows for spherical particles in Newtonian binders (Phillips et al., Koh et al., Sinton et al., and Hampton et al.). In this study, we have extended the model of Phillips et al. by especially incorporating the apparent slip condition at the wall for capillary and slit flows. Such wall slip effects are shown to be important in Couette (Jana et al.), Poiseuille and torsional flows (Kalyon et al., Yilmazer and Kalyon, and Aral and Kalyon). Our presentation will focus on the conditions at which particle migration effects are important and materials and flow conditions for which they are insignificant.

References:

Aral, B. and D.M. Kalyon, J. Rheol. 38, 957 (1994).
Chow, A.W., S.W. Sinton, J.H. Iwamiya, and T.S. Stephens, Phys. Fluids 6, (1994).
Gadala-Maria, F. and A. Acrivos, J. Rheol., 24, 799 (1980).
Hampton, R. E., A. A. Mammoli, A. L. Graham, N. Tetlow and S. A. Altobelli, J. Rheol. 41, 621 (1997).
Jana, S. C., B. Kapoor and A. Acrivos, J. Rheol. 39, 1123 (1995).
Kalyon, D.M., P. Yaras, B. Aral, and U. Yilmazer, J. Rheol. 37, 35 (1993).
Koh, C.J., P. Hookham, and L.G. Leal, J. Fluid Mech. 266, 1 (1994).
Leighton, D. And A. Acrivos, J. Fluid Mech. 181, 415 (1987).
Phillips, R.J., R.C. Armstrong, R.A. Brown, A.L. Graham, and J.R. Abbott, Phys. Fluids A 4, 30 (1992).
Yilmazer, U. and D.M. Kalyon, J. Rheol. 33, 1197 (1989).

Symposium FS
Polymer Friction, Slippage, and Dynamics Near Surfaces

Organizer: Lynden Archer

Thursday 8:05 San Carlos III FS1

SLIP AND REDUCED NEAR-WALL MOBILITY OF AN ENTANGLED POLYMER MELT IN STRONG SHEAR FLOW

Geoffrey M. Wise[1], Morton M. Denn[1], Alexis T. Bell[1], Hermis Iatrou[2], and Jimmy W. Mays[2]

[1]Materials Sciences Div./Dept. Chemical Engineering, Lawrence Berkeley Nat. Lab & U. California at Berkeley, Berkeley, CA 94720-1462; [2]Department of Chemistry, University of Alabama, Birmingham, AL 35294

Using ATR/FTIR, we observe the replacement of isotopically-labeled polybutadiene (M~80,000 g/mol) near a flat zinc selenide surface by pressure-driven shear flow of unlabeled chains. At low shear stresses, the replacement of the labeled chains is consistent with no slip at the wall. At higher stresses, the initial replacement of labeled chains is faster than expected if the no-slip condition holds, while a transition to sluggish removal of labeled chains at long times suggests that near-surface chains have a decreased transverse mobility, perhaps caused by chain extension.

Thursday 8:30 San Carlos III FS2

MOLECULAR ORIGIN OF WALL SLIP AND POLYMER SURFACE INSTABILITIES

Vijay R. Mhetar, Tien Dao, and Lynden A. Archer

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122

We investigate apparent violations of the no-slip hydrodynamic boundary condition in melts and concentrated solutions of high molecular weight polymers under plane-Couette shear flow. Using a combination of micro-tracer particle velocimetry and a new surface polarimetry method, we demonstrate that apparent slip violations in entangled polymer fluids is caused by an unavoidable mismatch between polymer relaxation dynamics near solid surfaces and in bulk. A simple relationship between the critical shear stress for gross slip violations and the plateau modulus (a bulk material property), is shown to be accommodated by such dynamic mismatch between surface and bulk polymer molecules.

Thursday 8:55 San Carlos III FS3

SPURT FLOW OF POLYBUTADIENES AND POLYISOPRENES

Priyan R. Manjeshwar[1], Faith A. Morrison[1], and Jimmy W. Mays[2]

[1]Department of Chemical Engineering, Michigan Technological University, Houghton, MI 49931; [2]Department of Chemistry, University of Alabama, Birmingham, AL 35294

The spurt instability (a rapid increase in flow rate at a critical stress) occurs in stress-controlled capillary flow of high molecular weight polymer melts. This instability is one of many polymer-flow anomalies which are grouped under the heading of *melt fracture*. One of the difficulties in the study of melt fracture (and related wall-slip effects) is that a wide variety of phenomena are observed. By concentrating on the spurt effect, we hope to be able to pinpoint a fundamental cause of melt fracture.

Flow curves are reported for a series of polybutadienes and polyisoprenes which undergo spurt. The critical stress for spurt is found to vary slightly with molecular weight (τ_c(PB) ~$M^{-0.27}$, τ_c(PI) ~$M^{-0.17}$), contrary to the observations of Vinogradov et al. where for similar materials they found τ_c ~M^0 (*J. Polym. Sci.*, A-2, 10 1061 (1972)). The extrapolation length, b, as a function of molecular weight is found for PB to follow b~$M^{4.6}$ which is different from the b~$M^{3.4}$ predicted by Brochard and deGennes(*Langmuir*, 8, 3033 (1992)) and observed for HDPE by Wang and Drda (*Macromol.*, 29, 4115-4119 (1996)). The scaling b~$M^{3.4}$ is observed at high molecular weights in both our materials. The deviation at low molecular weights for PB is not unexpected since low-molecular-weight species would be expected to reduce the coil-stretch deformation which is responsible for slip in the Brochard and deGennes picture. Our spurt results are compared with other reports in the literature and put into context with the general study of melt fracture.

Thursday 9:20 San Carlos III FS4

INTERFACIAL STICK-SLIP TRANSITION OF MONODISPERSE POLYBUTADIENE IN CAPILLARY FLOW

Xiaoping Yang and Shi-Qing Wang

Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Four monodisperse polybutadienes(PBd) have been studied in controlled-pressure capillary flow as well as in oscillatory shear. The nature of the discontinuous flow transition in capillary flow, which was previously interpreted as a constitutive transition from "a fluid to a high-elastic state" [1], has been clarified for the first time. Dependence of the flow behavior on the surface condition and die diameter unambiguously indicates that the observed transition is an interfacial stick-slip transition (SST), identical in nature to the reported interfacial SST in polyethylene extrusion [2-3]. The critical stress for the SST is found to be molecular weight independent, and the magnitude of the SST as characterized by the extrapolation length b is found to scale with molecular weight to the 3.4 power.

To be published in Rheologica Acta.

[1] Vinogradov GV, Protasov VP, Dreval VE Rheol Acta 23:46-61 (1984).
[2] Wang SQ, Drda PA Macromol Chem Phys 198:673-701 (1997b).
[3] Wang SQ, Adv Polym Sci (1998).

Thursday 10:10 San Carlos III FS5

PRESSURE AND TEMPERATURE EFFECTS IN SLIT RHEOMETRY: IMPLICATIONS FOR SLIP MEASUREMENTS

Grant Hay, Kailash M. Awati, Yoosup Park, and Michael E. Mackay

Department of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

The slit die is a commonly used apparatus for the measurement of the constitutive response of polymer melts to shear deformation. Disadvantages of this technique are the generation of pressures well above atmospheric, probable shear heating and heat transfer away from the die. In the analysis of data obtained from a slit die it is usually assumed that the fluid is incompressible, shear heating is negligible, stress is constant along the die length and pressure has no effect on viscosity. It is known temperature and pressure effects cause pressure profile curvature and therefore the stress is a function of the die length. This has major implications when using the Weissenberg-Rabinowitsch (WR) shear rate correction. The stress used in the WR correction is calculated from the pressure gradient, hence any pressure profile curvature will affect this correction dramatically. We will show how such curvature can lead to divergence of the flow curves for different die gaps at the critical stress for slip mentioned in the literature. We present an approximate theoretical treatment of pressure and viscous heating effects on the flow of a power law fluid through a slit die. It is assumed that the flow remains one dimensional, and this approximation compares well for pressures typically achieved in the laboratory when checked via finite element simulations of the complete momentum and energy equations. This model offers a method of including pressure and viscous heating effects in the analysis of experiments and we will rationalise experimental pressure profiles for LLDPE. It will be shown that slip velocities measured with a reducing gap parallel plate technique at comparable rates to that in the slit die are negligible in the analysis of slit die data.

Thursday 10:35 San Carlos III FS6

RHEOLOGY OF POLY (LACTIC ACID) : HIGH SHEAR STRESS SLIP AND GENERAL VISCOELASTIC BEHAVIOUR

Justin J. Cooper-White and Michael E. Mackay
Department of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

Poly (Lactic Acid), or PLA, polymers and associated copolymers have recently been projected as biodegradable replacements for conventional thermoplastics. Although currently these polymers are high cost, and solely used for biomedical applications, recent developments of a continuous process for the manufacture of polylactides have made them potentially competitive with polyolefins. Easily synthesised from renewable raw materials, the physical and mechanical properties of these polymers rival those of many conventional petrochemical plastics, yet little is known of the fundamental flow behaviour of PLA melts. PLA has three isomeric forms, poly (levo-lactic acid) and poly (dextro-lactic acid), which are both semi-crystalline in nature, and poly (meso-lactic acid) or poly (d,l-lactic acid), which is amorphous. In this paper, we provide the results of dynamic and steady shear tests on high molecular weight PLAs, utilising parallel plate rheometry. The viscoelastic properties of PLA melts, of varying molecular weights, were measured over a range of temperatures, frequencies and shear rates. The characteristic parameters of the terminal region, such as zero-shear viscosity, elasticity coefficient, and equilibrium compliance were determined, and their dependencies on molecular weight and temperature are discussed. In addition, polymer chain parameters, including the molecular weight between entanglements, entanglement density, and the characteristic ratio are calculated, with some interesting results. High shear tests performed at low gaps effectively extended the low steady shear results from large gap experiments. The high shear stress slip of these PLAs is determined at shear rates up to 120 1/s and gaps of 10 to 50 microns. The slip velocity of PLAs shows a monotonic increase with stress, as noted for other polymers. However, against a stainless steel surface, the slip velocities are far larger than those exhibited by conventional polymers, e.g. commercial LLDPE and monodisperse Polystyrene.

Thursday 11:00 San Carlos III FS7

WALL-SLIP AND POLYMER MELT FLOW INSTABILITY: ANALYSIS AND MODELING

William B. Black and Michael D. Graham
Department of Chemical Engineering, University of Wisconsin-Madison, Madison, WI 53706

We will describe efforts to combine modeling of slip at polymer-solid interfaces with analysis of the stability of viscoelastic shear flow, to better understand how slip and viscoelasticity might interact to lead to the various instabilities observed in polymer melt flow processes. In the limit of high Weissenberg number and small but nonzero slip velocity, we find that even a very weak dependence of slip velocity on the elastic normal stress (in the flow direction) leads to short wavelength instability of viscoelastic shear flow of the upper convected Maxwell fluid. We emphasize that this is not a ``constitutive instability" - both the bulk and interfacial constitutive equations are monotone - but rather a dynamical instability due to the interaction of slip and viscoelasticity. If the slip velocity is independent of normal stresses, then the flow is always stable. These analytical results are restricted to the UCM model, but are independent of the specific form of the model for slip. Numerical results for specific slip models and the Phan-Thien-Tanner bulk constitutive model show that the results are robust in the presence of nonlinear viscoelasticity. One possible origin of a normal stress dependence of the slip is an anisotropic friction tensor for chains adsorbed to the wall, which arises from the idea that disentanglement is easier the more stressed the network is. Rigorous application of this analysis to a die exit region has not yet been achieved. Nevertheless, because of the high stresses there, it is in this region that the instability predicted by our analysis would first be expected to arise.

Thursday 11:25 San Carlos III FS8

A BROWNIAN DYNAMICS STUDY OF SOLVENT QUALITY EFFECTS ON POLYMER BRUSHES

Thomas Kwan[1], Eric Shaqfeh[1], Phillip Schorr[2], and Matthew Tirrell[2]

[1]Dept. of Chemical Engineering, Stanford University, Stanford, CA 94305-5025; [2]Dept. of Chemical Engineering, University of Minnesota, Minneapolis, MN 55455

Polymer brushes present a very different kind of system when compared to free polymers in solution, but it is one in which solvent quality also plays an important role. We shall present results from large-scale Brownian dynamics simulation of the effect of flow on the conformations of polymer brushes in good and theta solvents. In the good solvent case, oscillatory shear flow at different shear rates, frequencies, and brush compression has been applied. Two distinct brush regimes emerge with the strain amplitude as the critical parameter. At small strain amplitudes, the equilibrium brush behavior is recovered, while at high strain amplitudes, steady shear behavior is obtained. In crossover between the two regimes we find and interesting brush response that is dependent on the size of the tethered chains and the degree of brush compression. In the theta solvent case, steady shear flow at various shear rates was simulated. The normal and friction forces are calculated and contrasted to those of a brush in a good solvent. In both cases, we compare to available experimental data obtained using the surface force apparatus.

Thursday 11:50 San Carlos III FS9

FRICTION AND NANOINDENTATION OF CROSSLINK POLYAMIDE SURFACES

Suresh K. Ahuja[1] and Karl R. Yoder[2]

[1]Materials, Xerox Corporation, Webster, New York 14580; [2]Department of Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

Friction and wear of polymer surfaces depend on modulus, hardness and damping properties of surfaces. Polyamides, polycarbonates, and polyesters were made into coatings on aluminum substrate and died at 110C for half an hour. The polymer surfaces were indented by a conical diamond tip of a nanoindenter. From loading and unloading curves as function of displacement, modulus and hardness were determined for crosslinked and uncrosslinked polyamides and compared to polyester and polycarbonate. Both surface modulus and hardness increase by as much as a decade as the polyamide is crosslinked. Modulus and hardness is found to decrease as the depth is increased. The results are analyzed in terms of surface morphology and defects in these surfaces which are then correlated to surface friction.

Symposium EM

Rheology and Microstructure of Electro and Magneto-Rheological Fluids

Organizer: Jon Bender

Thursday 8:05 San Carlos II EM5

FLOW OF MUTICOMPONENT SUSPENSIONS UNDER HIGH ELECTRIC FIELD

Steven W. Henley

Macromolecular Science & Engineering, University of Michigan, Ann Arbor, Michigan 48105

ER fluids do not seem to shear uniformly under high fields,but rather develope slip planes.These slip planes seem to be either delayed in their formation or interferred with through the addition of small amounts of various secondary particles with different physical,mechanical,or chemical properties.The addition of specific combinations of these secondary particles seems to enhance the properties of certain ER. fluids

Thursday 8:30 San Carlos II EM6

STUDIES OF ELASTOMERS FEATURING HIGH ELECTRORHEOLOGICAL RESPONSE

Bo Liu[1] and Montgomery T. Shaw[2]
[1]Polymer Program, Institute of Material Science, University of Connecticut, Storrs, CT 06269; [2]Dept. of Chemical Engineering & Inst. of Material Science, University of Connecticut, Storrs, CT 06269

Electrorheological (ER) materials have attracted considerable attention due to their "smart" behavior. One class of ER materials -- ER elastomers exhibits changes in modulus with electrical fields and has potential application in damping and electrical-mechanical control. In this paper, we present rheological studies of model elastomers based on silicone chemistry loaded with different types of ER active particles under DC and AC fields, as a function of particle concentration, water content, electrical field intensity and frequency. The rheological properties of such elastomers under the influence of an electrical field are modeled by an empirical equation: $G'_{app}(E) = G'_{0,\,app}[(1 + (E/E_0)^{\alpha}]$, where $G'_{app}(E)$ is the apparent shear modulus at an electrical field of E, $G'_{0,\,app}$ is the apparent modulus without field, and E_0 is the threshold value of electrical field intensity to obtain ER response. We also discuss the relationship between the microstructure and rheological behavior of those ER elastomers and their dependence on preparation conditions.

Thursday 8:55 San Carlos II EM7

THE RHEOLOGY AND MORPHOLOGY OF ELECTRORHEOLOGICAL(ER) DISPERSIONS USING AN ER ACTIVE POLYMER SOLUTION MATRIX

Greg P. Quist and Frank E. Filisko
Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48105

In many ER dispersions, an increase in the electric field induced viscosity can be facilitated by using a poly(n-hexyl isocyanate) solution as the continuous phase (i.e. matrix). This enhancement is generally greater than if the poly(n-hexyl isocyanate) solution simply added its ER activity to that of the dispersed particles. This unexpected synergistic enhancement has been linked to morphology changes in the polymer solution matrix due to increased electric fields between particles. In this study the electrorheology of several dispersions and the morphology of the poly(n-hexyl isocyanate) solution matrix in each case has been observed relative to the dielectric constant of the dispersed particulate phase. Additional investigations into the electrorheology and morphology of the poly(n-hexyl isocyanate) solutions has been performed (with no dispersed phase). Since poly(n-hexyl isocyanate) can become liquid crystalline at high concentrations in many solvents, this portion of the study investigated solutions in the isotropic, biphasic and fully liquid crystalline concentration regimes.

Thursday 9:20 San Carlos II EM8

MAGNETORHEOLOGICAL BEHAVIOR OF AN INVERSE FERROFLUID

Jorrit Mellema[1], Berend Jan De Gans[1], Cor Blom[1], and Albert Philipse[2]
[1]Department of Applied Physics, University of Twente, Rheology Group, Enschede, Netherlands; [2]Van 't Hoff laboratorium, University of Utrecht, Utrecht, Netherlands

Magnetorheological fluids are colloidal suspensions of magnetisable particles. Their rheology can be tuned externally: In the absence of a magnetic field they show liquidlike behaviour, whereas in the presence of a magnetic field solidlike behaviour is observed. The physical mechanism behind this transition is the formation of a chainlike network of dipolarly interacting magnetisable particles.

Similar behaviour can be observed in a suspension of non-magnetic particles in a magnetisable ferrofluid. Such systems, usually referred to as inverse ferrofluids, have the advantage that they are very well defined with respect to shape and size, making them very well suited for modelstudies. We used monodisperse silica spheres as non-magnetic colloids, having a radius of 200 nanometers. As the ferrofluid particles have a radius of only 7 nanometers the silica spheres can be seen as if moving in a continuous magnetisable background.

Of this system we have investigated the linear viscoelastic and flowproperties. We found that the storage modulus is at least an order of magnitude larger than the loss modulus for all cases studied, and has an almost constant value

over four decades in the frequency range. The storage modulus scales in first order linearly with volume fraction and quadratically with the magnetisation of the surrounding ferrofluid.The flow curves show Bingham-like behavior. The results can be understood in terms of a model that treats the particles as point dipoles that form gapspanning non-interacting chains. In the case of the linear viscoelasticity measurements the chains are supposed only to deform affinely. The viscosity measurements can be explained in terms of flow units of fragments of broken chains, whose characteristic size is determined by hydrodynamic and magnetic torques.

Symposium JA
Jet Breakup, Atomization, and Spraying of Non-Newtonian Liquids

Organizers: Chuck Manke and David V. Boger

Thursday 10:10 San Carlos II JA1

CAVITATION AND THE STATE OF STRESS IN A FLOWING LIQUID

Daniel D. Joseph
Dept. Aerospace Engineering & Mech., University of Minnesota, Minneapolis, MN 55455

The problem of the inception of cavitation is formulated in terms of a comparison of the breaking strength or cavitation threshold at each point of a liquid sample with the principal stresses there. A criterion of maximum tension is proposed which unifies the theory of cavitation, the theory of maximum tensile strength of liquid filaments and the theory of fracture of amorphous solids. Liquids at atmospheric pressure which cannot withstand tension will cavitate when and where tensile stresses due to motion exceed one atmosphere. A cavity will open in the direction of the maximum tensile stress which is 45 degrees from the plane of shearing in pure shear of a Newtonian fluid. It is suggested that a cavitation mechanism for atomization is associated with high extensional stress at a point of separation near the nozzle entrance. Experiments which support these ideas are discussed and some new experiments are proposed.

Thursday 10:35 San Carlos II JA2

TAYLOR-MODE BREAKUP OF A POLYMERIC LIQUID JET

Shirley C. Tsai[1], Patrick Luu[1], Sylvia Tsai[1], and Gerald Roski[2]
[1]Chemical Engineering, California State University - Long Beach, Long Beach, CA 90840;
[2]Electrical Engineering, California State University - Long Beach, Long Beach, CA 90840

We have previously reported on a new spray technique called ultrasound-modulated two-fluid (UMTF) atomization [AIChE J., 3340-3350, 1996]. Specifically, a capillary wave is established on a liquid jet as it issues from a coaxial two-fluid atomizer, the nozzle tip of which vibrates at an ultrasound frequency. As the capillary wave travels downstream in the direction of air flow, it is amplified by the air blowing around it and then collapses into drops. The resulting drop-size distribution was found to peak at a drop diameter equal to the wavelength of the capillary wave generated by the third harmonic frequency. This finding is consistent with the effects of air velocity on the relative amplitude growth rates of capillary waves with different wavelengths based on the linear dispersion models of temporal instability first derived by G.I. Taylor and H. Jeffreys for wind-generated capillary waves. In this paper, we shall present flow visualization of a jet of dilute polymeric solution near the nozzle tip using a 30-ns pulse laser as a verification of the jet initial and boundary conditions. We have observed a bright band at the nozzle tip in both ultrasonic and UMTF atomization, but not in two-fluid atomization. The bright band can be attributed to scattering of laser light sheet by the capillary waves generated by the ultrasound on the liquid jet. A good agreement between the jet breakup time calculated from the band length and that predicted by the linear models of amplitude growth rates has led to the conclusion that UMTF atomization occurs via Taylor-mode breakup of capillary waves, and it can be used to control the drop-size and size distribution of two-fluid atomization for uniform drop formation.

* Supported by the National Science Foundation in the Division of Chemical and Transport Systems, Grant No. CTS 9601530

Thursday 11:00 San Carlos II JA3

THE EFFECT OF VISCOELASTIC POLYMERS ON DROP PRODUCTION IN AGRICULTURAL SPAYS

Vera Romagnoli[1], Phil Felton[2], and Robert K. Prud'homme[1]
[1]Department of Chemical Engineering, Princeton University, Princeton, NJ 08544; [2]Department of Mechanical Engineering, Princeton University, Princeton, NJ 08544

Agricultural spraying is problematic due to the production of small drops that drift from the intended target. In addition, viscoelastic polymers added to increase the drop size degrade in strong shear fields. Solutions sprayed from nozzles produce a distribution of drop sizes. The drop size distribution can be altered by changing the physical properties of the solution. Small additions of viscoelastic polymers primarily alter the drop size distribution by changing the extensional viscosity of the solution. The role of extensional viscosity in the spray process is determined by independently varying the shear and extensional viscosity of PEO solutions. In addition, Guar solutions are studied because of their resistance to shear degradation. All drop sizes are measured using the Malvern 2600 particle size analyzer.

Thursday 11:25 San Carlos II JA4

ATOMIZATION OF SELF-ASSOCIATING POLYMER AND POLYMER-SURFACTANT SOLUTIONS AND EMULSIONS

Sally M. Yurgelevic, Zeynep Ergungor, Esin Gulari, and Charles W. Manke
Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

Previous work has shown that high molecular weight polymers are effective as agents for modifying the droplet size distribution of mists and sprays. However, in industrial applications such as the control of machining fluid mist with high molecular weight polymers, mechanical degradation of the molecular weight of the polymer in shear flow limits the effective life of the additive. Self-associating polymer systems, where large-scale structures develop through physical associations of lower molecular weight polymer units, would seem to offer improved shear stability as mist-control additives. Here we examine the atomization behavior of two different types of self-associating polymer systems: a dilute styrene-butadiene-styrene triblock copolymer solution where differential solvent affinity of the blocks leads to styrene-styrene associations; and dilute oil-in-water emulsions with dissolved polyethylene oxide (PEO), which interacts with petroleum sulfonate surfactants used to stabilize the emulsions. Experiments performed with an air-blast atomizer and an optical particle sizer show that the styrene-butadiene-styrene polymer additive has little effect on atomization, apart from the expected dependence of droplet size on shear viscosity. This can be attributed to the fact that the styrene-styrene interactions induce the formation of isolated micelles in dilute concentration regimes, rather than highly elongated structures that would influence the droplet formation mechanism. In contrast, the PEO-petroleum sulfonate interaction produces a very strong antimisting effect, which is thought to result from surfactant micelles acting as bridges between neighboring PEO molecules and thereby building longer structures.

Thursday 11:50 San Carlos II JA5

DROP IMPACT ON SOLID SURFACES

Regan C. Crooks and David V. Boger
Dept. Chemical Engineering, University of Melbourne, Parkville, Victoria 3052, Australia

The impact of drops on solid surfaces is of importance in a number of industries. Examples of applications inclued spray cooling, ink jet printing and pesticide spraying. It is desirable to reduce splashing and promote spreading of drops on surfaces. To understand the mechanism of drops impacting on various surfaces, both a progressive scan video camera (at 50 frames per second) and a high speed camera (at 1000 frames per second) are used. Fluids have been constructed to observe the effects of shear viscosity, surface tension, and density. Experimental conditions have been adjusted to observe the effects of surface roughness, impact velocity, and drop diameter. A piezoelectric droplet generator is under construction to produce drops of varying diameters and velocities. These factors are reported in terms of the dimensionless groups: Reynolds number, Weber number and Ohnesorge number. We have also experimented with various polymers (included polethylene oxide and guar gun) to observe the behavior of viscoelastic fluids in drop impact. These fluids were constructed with a constant shear viscosity and similar

properties to that of some Newtonian fluids to observe the effect of extensional viscosity on drop impact. We are investigating a means of quantifying the effect of extensional viscosity on both spreading and splashing.

Symposium AN
Analytical and Numerical Solutions to Flow Problems

Organizer: Michael Renardy

Thursday 8:05 Los Angeles AN14

COMPUTATION OF TRANSIENT FLOWS OF DILUTE POLYMER SOLUTIONS THROUGH AN ABRUPT CONTRACTION USING THE ADAPTIVE LAGRANGIAN PARTICLE METHOD

Xavier Gallez, Pierre Halin, Roland Keunings, and Vincent Legat
CESAME Division of Applied Mechanics, Universite catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

The Lagrangian Particle Method (LPM) has been proposed recently [1] for the computation of transient viscoelastic flows using either a constitutive equation (macroscopic approach) or a kinetic theory model (micro-macro approach). In LPM, the polymer stress is computed at discrete Lagrangian particles which are convected by the flow, while the conservation equations are solved by means of a finite element technique. The polymer stress computation is achieved by solving along the particle trajectories either the macroscopic constitutive equation or the stochastic differential equation for a particular kinetic theory model. In the present paper, we present the Adaptive LPM (ALPM) where the Lagrangian particles are automatically and continuously created or deleted when and where needed. ALPM is applied to the start-up flow through an abrupt contraction. Results are given for the Warner Finitely Extensible Non-Linear Elastic (FENE) dumbbell model of a dilute polymer solution. They are compared to experimental data and to numerical results obtained with the FENE-P constitutive equation.

[1] P. Halin, G. Lielens, R. Keunings, V. Legat, "The Lagrangian Particle Method for Macroscopic and Micro-Macro Viscoelastic Flow Computations," accepted for publication in J. Non-Newt. Fluid Mech,. May 1998.

Thursday 8:30 Los Angeles AN15

SIMULATION OF THE DOI-EDWARDS MODEL IN COMPLEX FLOW

Antoon P.G. van Heel, Martien A. Hulsen, and Ben H. A. A. van den Brule
Department of Mechanical Engineering and Marine Technology, Delft University of Technology, Delft 2628 AL, Netherlands

Two methods to simulate the Doi-Edwards model in a complex flow field are compared. The first method is based on a configuration field approach (JNNFM 70 (1997), 79-101), combined with a stochastic algorithm that mimics the reptation process.

In the second method a new (isotropic) ensemble of tube segments (unit vectors) is created every time step. The actual distribution of every ensemble is calculated using the deformation gradient that maps the distribution at the moment of creation to the distribution at the current time. The relative weight of a particular tube ensemble to the stress is decreased, as the ensemble becomes older in the course of the simulation. The weight function follows from the probability for a segment to survive for a certain period of time.

The flow problem we selected is the flow past a cylinder confined between two flat plates. It is shown that the second method is very efficient and has clear advantages over the first, more traditional, method.

Thursday 8:55 Los Angeles AN16

EXPERIMENTAL OBSERVATION AND NUMERICAL SIMULATION OF PLANAR FLOW WITHIN A CONFINED SLIT FOR MOLTEN POLYETHYLENE

Rui-Feng Liang[1], Jin Wang[1], and Malcolm R. Mackley[2]
[1]Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China; [2]Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, United Kingdom

We report experimental observations and numerical simulations of the planar flow with a confined slit for two low-density polyethylenes and two high-density polyethylenes with different molecular structure. The four melts are rheologically characterized in simple shear on a Rheometric RDSII rheometer with two parallel plates of a gap 1mm at a temperature of 190C, in terms of a Wagner integral constitutive equation. The discrete relaxation time spectra are determined from data of linear viscoelasticity and the exponential damping function coefficient from data of linear and non-linear relaxation moduli obtained from step strain experiments. The planar flow with a confined slit of contraction ratio of 10:1 has been achieved on a Multipass Rheometer II which has been recently developed by Dr. Mackley and his team. The apparatus is a capillary rheometer with two hydraulic driven pistons which force material upwards or downwards through a detachable central test section where the slit is confined between two glass windows and the test material is contained within a fully enclosed environment at 190C. The global stress field is experimentally characterized using flow birefringence technique for each polymer melt at 5-10 different flow rates and then quantitatively described in terms of stress-optical law. These results are further compared with numerical simulations obtained by using a finite element software package, Polyflow, with experimental flow boundary conditions. The flow behaviour will be addressed in relation to their molecular structure. The consistency between numerical simulation results and experimental results will be discussed and compared to our previous work published in J. Non-Newtonian Fluid Mech., 59 (1995) 129-153.

Thursday 9:20 Los Angeles AN17

MODELING THE RHEOLOGY OF SUSPENSIONS OF SPHERICAL PARTICLES WITH ADSORBED POLYMERS

Kai Zhang and Charles W. Manke
Dept. Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

The rheology of suspended particles with adsorbed polymers is important to applications such as automotive lubricants, where dispersant polymers are employed to inhibit the agglomeration of soot and other particles that form during the service life of motor oils. Here, we have employed Dissipative Particle Dynamics (DPD), a new mesoscopic dynamical simulation technique, to model the rheology of spherical particles suspended in a solvent, with polymer chains adsorbed to the surface of the particles. Interactions among the various species present in this system have important effects on the overall rheological behavior, and the DPD model provides an explicit representation of the polymer-solvent, polymer-particle, and particle-particle interaction forces. Calculations are performed to show the effects of these interactions on rheological properties in steady shear flow.

Thursday 10:10 Los Angeles AN18

THE VISCOPLASTIC FLOW ANALYSIS OF COLD EXTRUDED CHOCOLATE

Nita C. Mulji and Malcolm R. Mackley
Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, United Kingdom

The cold extrusion processing of chocolate, where solid chocolate is isothermally extruded below its normal melting range, was first reported by Beckett et al. (1994). The material deformed plastically, as it was forced through an area reduction in a die, and a time dependent post extrusion plasticity was observed where the product hardened over time to its normal brittle state. A key benefit of this process is the ability to produce a diverse range of extrudate shapes. This paper presents some experimental, theoretical and numerical results obtained for the axisymmetric cold extrusion of chocolate. Chocolate can be usefully modelled as a rigid-plastic solid because of the existence of yield behaviour. The constitutive model used requires only one material parameter, the uni-axial yield stress for which a value has been obtained from the experimental data. In general, this is a function of temperature and chocolate composition. ABAQUS v5.5, a commercial finite element package, has been used to estimate the extrusion pressure

for a variety of die geometries. The numerical simulation results have been shown to lie between lower and upper bound theorem predictions for dies with no die land. In particular, the effect of area reduction, die land length and flowrate on the extrusion pressure has been studied. Experiments showed that the wall boundary condition varied as the area reduction was increased. A closer examination of the results showed that the wall shear stress was constant for large area reductions and varied for the smaller area reductions.

Thursday 10:35 Los Angeles AN19

FINITE ELEMENT SIMULATIONS OF VISCOELASTIC POROUS MEDIA FLOWS

Felix Alcocer and Pushpendra Singh
Mechanical Engineering, NJIT, Newark, NJ 07102

The FENE dumbbell model is used to study the viscoelastic porous media flows. The domain is discretized using the finite element method and the porosity used is held around 40%. By changing the model parameters the role of relaxation time and the molecular weight is investigated in determining the pressure drop. Simulations show that the pressure drop for the viscoelastic case is much higher than for a Newtonian fluid with the same zero shear viscosity and that it also depends on the relative arrangements of the particles, i.e., for the same porosity the pressure drop is much larger for some configurations. The pressure drop is higher for the viscoelastic fluid the same zero shear viscosity because the macromolecules become highly stretched in the narrow pores which causes a much greater pressure drop.

Thursday 11:00 Los Angeles AN20

COMPUTER SIMULATIONS OF FLOWING BEHAVIOR OF PARTICLES IN THE ASYMMETRICAL HOPPER BASED ON DISCRETE ELEMENT METHOD

C. S. Chou[1], L. J. Chiang[1], J. Smid[2], J. T. Kuo[2], and S. S. Hsiau[3]
[1]Mechanical Engineering, National Pingtung University of Science and Technology, Pintung 91207, Taiwan; [2]Mechanical Engineering, National Taiwan University, Taipei 10617, Taiwan; [3]Mechanical Engineering, National Central University, Chung-Li 32054, Taiwan

By employing the theory of a stack of particles in the asymmetrical hopper, the initial coordinates of the particles and the boundary of the hopper are defined. By making use of the discrete element method model, the path, flow pattern and velocity fields of the disks in the asymmetrical hopper are studied numerically. Three kinds of asymmetrical hoppers ((i) LA=15°, RA=40° ; (ii) LA=15°, RA=30° ; (iii) LA=15°, RA=20°) are used to contain 100 disks of 1 cm diameter, respectively. LA is the angle between the left boundary of the hopper and a vertical line, and RA is the angle between the right boundary of the hopper and a vertical line. The results of our computer simulation show that the hopper boundary affects the flowing behavior of the disks. The research work reported here shows that the disks close to the right hopper boundary move more slowly and develop a quasi-stagnant zone. The numerical results reported here, along with experimental results, provide fundamental and important information for designing moving granular bed flue gas cleanup filters.

Thursday 11:25 Los Angeles AN21

MIXING OF TWO-PHASE FLUIDS

Patrick D. Anderson, Gerrit W. Peters, Frank P. Baaijens, and Han E. Meijer
Department of Mechanical Engineering, Eindhoven University of Technology, Eindhoven 5600 MB, Netherlands

The complexity of chaotic mixing processes has led to several simplifications in the analysis of mixing. The geometry is considerably simplified and the rheology of the fluid is assumed Newtonian. Also the mixing of two similar but immiscible fluids is considered and diffusion is assumed neglectable. The interface then becomes passive and the computational analysis of mixing results in a post-processing operation. First, knowledge about the kinematics is required and after this several dynamical tools can be used to analyze the mixing efficiency. Here we present results for mixing simulations where some of the above simplifications are dropped. Mixing of dissimilar (immiscible) fluids in a two- and three-dimensional prototype (cavity) mixing flows is considered. A high order spectral element method is used for spatial discretization and a projection scheme for temporal discretization. To follow the interface an adaptive front tracking technique is applied. The influence of the difference in rheological behavior between continuous and disperse phase on the generation of interfacial area is studied. The method also opens the future possibility to study the rheology of the mixture.

Thursday 11:50 Los Angeles AN22

AN OBJECTIVE ROTATION TENSOR USED IN CONSTITUTIVE EQUATIONS FOR VISCOELASTIC FLUIDS

Lewis E. Wedgewood
Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607

To develop objective constitutive equations, local frames which translate and rotate with the fluid particle can be used. For example, the corotating frame rotates such that the curl of the velocity calculated in this frame vanishes. From the corotating frame, the Jaumann derivative can be derived. In this paper, a new local frame is developed which causes the cross product of the velocity and acceleration to vanish and is designated as the rigid-rotating frame. The corotating and rigid-rotating frames rotate identically for a rigid-body rotation of the fluid, but rotate differently in flows that contain shearing. This difference in rotation can be used to develop an objective rotation tensor that can be applied to constitutive equations for viscoelastic liquids. An evolution equation for this objective rotation tensor is derived and is solved for several flows. The rigid-rotating frame can also be used to develop a rheological time derivative which has been designated the rigid-rotational derivative. These new quantities expand the traditional set of kinematical variables and invariants available for use in constitutive equations. Use of this expanded set of kinematic variables is demonstrated in limiting constitutive equations. These constitutive equations demonstrate enhanced sensitivity to flow type. Applications to fluids with microstructure are discussed.

Author Index