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Symposium PO
Poster Session

Organizer: Susan J. Muller

Wednesday 5:30 Main Foyer PO1

SQUEEZING FLOW TESTING

Donald A. Becker[1], **Christopher W. Macosko**[2], **and Charles L. Rohn**[3]
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Squeezing flow between two parallel plates has some advantages over rotational shear testing. In spite of the wide range of sample geometries available with rotational rheometers, there are many materials that can be tested more easily in squeezing flow. For example, greasy food doughs, soap, waxy cosmetic products tend to exhibit wall slip, unstable suspensions and gels may produce a liquid film at the boundary of the upper plate, and some fiber reinforced prepregs may not give useful data when tested in torsion. Both unlubricated and lubricated squeezing flow measurements can give meaningful data. Unlubricated tests many relate to compression molding and vacuum forming. Lubricated squeezing flows can be used to measure biaxial extensional viscosity. This is a valuable test for food doughs For this reason Rheometric Scientific, Inc. has added this mode of testing to the ARES melt rheometer. Measurements can be made at both constant force and constant linear and Hencky strain rates covering a wide range of temperatures. Unlubricated squeezing flow measurements of PDMS will be presents at this poster session. These data are analyzed by the methods suggested by Laun (Laun. H. M. Angew, Makromol. Chem. Symp.1992, 56, 55; J. Non-Newtonian Fluid Mechanics, 1998).

Wednesday 5:30 Main Foyer PO2

SLIDING PLATE MICRO-RHEOMETRY OF POLYMER MELTS

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An experimental instrument capable of opto-mechanical studies of the rheology of thin polymeric fluid films is described. The apparatus probes the 'meso-scale' (length scales of O(μm)) and therefore bridges the gap between molecular-scale devices such as the Surface Force Apparatus (SFA) and conventional rheometers which characterize the 'bulk' rheological properties of non-Newtonian fluids. The parallel plates of the device consist of polished optical flats (flat to within lambda/4) The translating plate is mounted on a double cantilever spring system and imposing a lateral force results in a planar Couette motion within the plane of the springs provided the deflection is very much less than the lever arm. The instrument rigidity is carefully designed and calibrated to ensure it does not dominate over the sample properties - for this reason we use an electromagnetic drive system (with a speaker coil and a rare earth magnet) plus weak leaf springs. This allows us to study the static and dynamic properties of much lower viscosity materials than would be possible using piezoelectric "bimorphs". The device operates in a controlled stress mode and inductive sensors are used to track the motion of the surface. The instantaneous stress and strain can be extracted to within ±5 mPa and ±5 nm respectively for gaps in the range 1 - 50 μm. Alignment of the surfaces can be achieved by a three point adjustment using high accuracy micrometers. Transmission interferometry through the optically-transparent plates allows the parallelism and absolute gap to be determined. The device utilizes small fluid samples, allows a wide range of molecular weights (and thus viscosities) to be investigated, and can be used with different substrate materials & surface coatings. We use the device to explore the changes in the rheology of entangled PDMS melts in small- and large-amplitude oscillatory motions as the plate separation is progressively decreased.

Wednesday 5:30 Main Foyer PO3

THE CONTROLLED NEEDLE VISCOMETER-A NEW RHEOLOGICAL PROPERTY MEASUREMENT SYSTEM

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A new controlled needle viscometer(CNV) has been developed to accurately measure viscosities of Newtonian and non-Newtonian fluids. The CNV includes a vertical sample tube filled with the liquid of which the viscosity is to be determined and a controlled needle which is pushed down through a fluid sample using external weights. Using a needle guide at the top of the sample insert tube, the conrolled needle having a known density is made to fall through the liquid in the sample tube. Using the time that the controlled needle takes to fall between two known distance transducers, the velocity of the controlled needle falling through the liquid is determined. Thus, the viscosity can be calculated by using the velocity of the controlled needle.

Wednesday 5:30 Main Foyer PO4

THERMAL EXPANSION OF THE FORCE REBALANCE TRANSDUCER IN A RHEOMETRIC SCIENTIFIC ARES ROTARY RHEOMETER

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The force rebalance transducer (FRT) uses an active control system of magnetic fields to hold the core of the transducer in a fixed position against an applied torque or normal force. The magnitudes of the applied torque and normal force are calculated from the current supplied to the magnets to hold the core fixed. This system has the advantages of excellent stability about the zero position and low compliance in the transducer. However, if the torque or normal force is large and is applied for a length of time, the current required to hold the transducer core can lead to significant heating of the transducer. Previous measurements on a force rebalance transducer in a Rheometric Scientific RMS-800 rotary rheometer indicated that the heating causes a significant thermal expansion which could introduce significant errors in measurements of normal forces (Niemec et al, J. Rheology, Vol. 40, pp. 323-334, 1996). Rheometric Scientific has redesigned the FRT to use components made of Invar (a metal with a very low coefficient of thermal expansion). In tests similar to those performed on the previous model of the FRT, we find that, while the problem has been reduced, it has not been entirely eliminated. One interesting feature is that an applied torque causes the transducer to first extend and then retract, reflecting different time scales for heating the transducer core and the external shell. The importance of the thermal effect on rheological measurements will be discussed.

Wednesday 5:30 Main Foyer PO5

A NONLINEAR FLUID STANDARD REFERENCE MATERIAL: PROGRESS REPORT

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NIST is in the process of producing a new Standard Reference Material (SRM 2490 Nonlinear Fluid for Rheological Measurements) that replaces the previous SRM 1490 Nonlinear Fluid Standard. NIST produces Standard Reference Materials for the purposes of calibrating instruments and for use in research into better measurement techniques. The new polymer solution SRM should be useful to the polymer processing community, as it will have well-characterized shear thinning behavior and first normal stress differences over a range of strain rates and temperatures. In conjunction with the development of the fluid, NIST is organizing a round robin study of the fluid to help equipment manufacturers and researchers in different laboratories to better understand the inherent lab-to-lab variability in their measurements and consequently help reduce these. This study will also ensure that the chosen material properties are acceptable to those participating in the round robin, which is important from the point of view of making the fluid commercially viable. SRM 2490 will consist of polymeric polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (also called pristane); this material will have a much wider temperature range than the previous SRM 1490, and should also be somewhat more stable. NIST will certify the fluid for the shear-rate dependence of viscosity and first normal stress difference over a temperature range of approximately 50 C. The linear viscoelastic responses will also be certified along with the temperature dependence of the shift factors and the zero-shear-rate viscosity. Here we present progress up to the current time.

Wednesday 5:30 Main Foyer PO6

EVALUATION OF THE VISCOSITY PRESSURE COEFFICIENT USING TWO METHODS

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The effect of pressure on the viscosity of molten polymers is usually modeled by an exponential function. For example, the viscosity of a power-law fluid can be represented by $\eta = K \exp(\delta P)\gamma^{n-1}$, where δ is the viscosity pressure coefficient. In capillary flow, the effect of pressure on viscosity results in the upward curvature of the data in the Bagley plot. Laun (*Rheol. Acta*, 22, 1983) presented a simple method to evaluate the pressure coefficient by analyzing capillary flow data. We have used this method to calculate an approximate value of δ for a LLDPE at 150^{o}C, using dies of several L/D values (0 - 40). This calculated value is compared with the one obtained for the same material using a new high pressure sliding plate rheometer. This instrument was designed to generate simple shear flow under a homogeneous hydrostatic pressure, while measuring shear stress locally. The experimental techniques and results for both rheometers are discussed.

Wednesday 5:30 Main Foyer PO7

RHEO-OPTICAL FTIR SPECTROSCOPY OF POLYMER DYNAMICS

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Infrared spectroscopy is potentially a powerful tool to study the viscoelastic and the flow response of complex polymeric materials. In a FTIR spectrum, there is a characteristic vibrational absorption frequency (or finger print) for every chemical moiety (e.g. individual components of a multicomponent blend, or different regions of a micro-phase separated block copolymer). Therefore, by studying the anisotropy in the polarized spectra at different absorption bands (dichroism) during deformation, we can monitor the orientation behavior of several components simultaneously. We are developing a novel rheo-optical FTIR spectrometer, by taking advantage of the latest developments in rheometry, FTIR spectroscopy and polarimetry. To achieve this, we have combined a conventional rheometer, state-of-the art step-scan FTIR spectrometer, and polarization modulation optics. Using this apparatus, we are studying the orientation dynamics of complex polymer blends and block copolymers over a wide range of temperatures. The potential of the instrument will be demonstrated using a model polyurethane elastomer film.

Wednesday 5:30 Main Foyer PO8

MODELLING LDPE MELT RHEOLOGY WITH THE POM-POM MODEL

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The melt rheology of low density polyethylene (LDPE) is made distinctive by its extreme extension hardening in elongational flow geometries in contrast its equally strong thinning behaviour in shear. Traditional constitutive equations (e.g.K-BKZ) have been unable to describe simultaneously its rheological properties, particularily in planar extensional flow. A recent constitutive equation, derived from molecular considerations (the "pom-pom" equation) does capture the qualitative rheological behaviour of LDPE in shear and extension for the first time. Polymer melts with the specific pom-pom molecular have theoretically similar behaviour to LDPE due to its multiple branch

points. We use a hypothetical melt of pom-poms with different numbers of arms to model the behaviour of LDPE. The linear relaxation spectra for various LDPE samples is mapped to the distribution of backbone relaxation times of the pom-pom modes. Data from startup flow in uniaxial extension is used to fix the non-linear parameters of each mode. Predictions are then available with no further free parameters in shear and planar extension. These agree well with data from the literature and from our own measurements on commercial LDPE. The method suggests a concise and functional way of characterising long chain branching in polymer melts.

Wednesday 5:30 Main Foyer PO9

STOCHASTIC SIMULATIONS OF A FULL-CHAIN MODEL FOR THE LINEAR VISCOELASTICITY OF ENTANGLED POLYMERS

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A new stochastic algorithm, which accounts for the effects of segment connectivity, chain length fluctuations and constraint release, is proposed and used to simulate the linear viscoelastic properties of entangled polymers. Results, such as the scaling laws of zero-shear-rate viscosity and steady-state compliance, the relaxation and dynamic moduli, for both the linear and star polymers are shown and compared to experiments.

Wednesday 5:30 Main Foyer PO10

CRITICAL TESTS OF POLYMER DYNAMICS AND THE VISCOSITY PROBLEM

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The Ripple experiments by Welp et al (Macromolecules 1998) have confirmed the Reptation model as the correct model to describe the dynamics of linear polymer melts. The 3.4 exponent for the molecular weight dependence of the zero shear viscosity was found to be determined by a new mechanism, Vector Percolation.

Wednesday 5:30 Main Foyer PO11

VERIFICATION OF THE CCR MODEL: LINEAR AND STAR POLYMERS

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New binary interaction models that incorporate chain retraction, reptation and tube length fluctuations into a universal constitutive formalism have been developed for polydisperse linear and star polymers. The properties of these models are explored and compared in step strains and steady simple shear flow where we derive the Cox-Merz rule relating the steady shear viscosity with the linear viscoelastic dynamic viscosity. Empirical relationships between the linear viscoelastic material functions and the nonlinear material properties are shown to be a consequence of convective constraint release. The specific feature of CCR that allows this is that the rate of convective constraint release is proportional to the shear rate, γ. Theoretical predictions are quantitatively compared to experimental data for star and linear polymer systems.

Wednesday 5:30 Main Foyer PO12

RHEOLOGICAL BEHAVIOR OF CHEMICALLY MODIFIED POLYETHYLENES

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The rheological properties of commercial high (HDPE), linear-low (LLDPE) and low density (LDPE) polyethylenes modified with diethylmaleate (DEM) and 2,5dimethyl2,5di(tert-butylperoxyhexane) (Interox) in one case and with

Interox only in the other case were comparatively studied. The modification was carried out in a corotating twin screw extruder. The peroxide was added always in the same feed port. At that point, the polymer was already melted, and the monomer was well mixed in the polymer, in the case where both reactants were employed. The extrusion conditions employed ensured the complete decomposition of the peroxide. Additionally, nitrogen was used throughout the extrusion process, in order to keep an inert environment inside the extruder. Similar procedure was followed without using nitrogen to analyze its role in the polymer modification during processing. No previous studies have been found in the literature dealing with the use of different environments such as nitrogen during the functionalization via extrusion.

When peroxide was incorporated into HDPE and LDPE in a non controlled environment (air), the viscosity and the weight average molecular weight (Mw) increased due to an enhancement of the high molecular weight tails of the molecular weight distributions. However, when nitrogen was used, just a small increase in G" was obtained, as a consequence of a probable increase of long branches. The functionalization of both polyethylenes in nitrogen did not produce any changes in their rheology, while an increase in G" due to a probably increase in long chain branching resulted from the functionalization process in air. Concerning the LLDPE, a long chain branching mechanism may have taken place when peroxide was used in both environments, leading to a rise in G". Functionalization via extrusion caused an enlargement in the high molecular weight tails of the distribution, specially in air, which in turn led to higher values of η_o and G".

Wednesday 5:30 Main Foyer PO13

PRESSURE CHARACTERISTIC FOR NON-ISOTHERMAL FLOW OF THE THERMOPLASTIC POLYMERS MELTS IN CIRCULAR CONFUSER

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Melts of some polymers within the alteration of processing parameters are alike high-viscosity liquids with Arrhenius dependence of viscosity on temperature, their flow takes place in condition of the big gradients of the temperature and viscosity. Therefore it is necessary with investigation of such fluid flows to take into account both dissipation and heat exchange at boundary of confuser. To solve this conjugated problem the region of flow is separated into N concentric conical layers in confuser and it is assumed that viscosity over cross-section of each layer is constant and equal to one taking for average temperature over cross-section of this layer. Owing to this method the set of equations of motion and heat transfer is reduced to the set N+1 ordinary differential equations for the mean temperatures in layers and mean pressure and analytical expressions for components of velocity, dissipation function and heat transfer coefficients between layer. The effects connected with the dissipation of mechanical energy become dominated on some distance from entrance. It carries out to appearance of small viscosity high-temperature shear layer and to the pressure gradient which is less than for isothermal flow. On small flow rate the pressure characteris-tic is linear for adiabatic flow. With increase of flowrate the small viscosity layer appears at the exit from confuser in consequence of mechanical energy dissipation. The pressure gradient on the exit is considerably decreased in comparison with the isothermal flow that leads to nonlinear pressure drop-flowrate dependence. For confusers with small angle of opening high-temperature shear layer will have been extended almost on all confuser beginning in some flow rate. The pressure drop for this flow is decreased beginning and pressure characteristic with the flow of melts of thermoplastic polymers is non-monotonous. Pressure drop-flowrate dependence was investigated for different intensity of heat exchange with ambient too.

Wednesday 5:30 Main Foyer PO14

A NEW MODEL FOR THE AMORPHOUS PHASE OF POLYMERS

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We review the present understanding of the properties of the amorphous phase of polymers, below Tg, above Tg and in the melt, and find it incompatible with abundant and confirmed experimental evidence by Low Raman spectroscopy, SAXS, Thermal Stimulated Current, specific volume, DNS, NMR, Brilloin scattering etc., which point to the existence of an inhomogeneous packing density at least at the nanometric scale, and which we postulate results from the interactive coupling between the bonds belonging or not to the same macromolecules. We show that

such a non homogeneous amorphous phase is in fact responsible for visco-elastic effects and rubber extensibility, which should no longer appear to be the direct consequence of the existence of the long and entangled chains. We develop a new statistical model, the EKNET statistics, which is used to explain why random coils inter-penetrate each other without much change of the rms end to end dimension, essentially because a minimization principle organizes the interactions between the bonds heterogeneously and create not only locally but also globally (in the rubber state) packed structures with "free volume" within the local and global packs and at their interface. The new model leads to a different understanding of the properties of polymers, which we call "Poly-conformer Physics".

Wednesday 5:30 Main Foyer PO15

BIREFRINGENCE AND VISCOELASTICITY OF LOW MOLECULAR WEIGHT POLYSTYRENES AROUND THE GLASS TRANSITION ZONE

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The complex strain-optical coefficient and the shear modulus for low molecular weight polystyrenes were measured around the glass transition zone. The molecular weights (M = 10,500, 5,970, 2,630, and 1,050) were close to or higher than the Rouse segment size (M =850) but less than the entanglement size (M =18000); the segment number per chain, N, was covered from 1 to 12.

For the lowest M sample, the frequency dependence of the modulus was similar to that for low M glass formers: No polymeric mode such as the Rouse modes was detected. The birefringence for the lowest M sample was found to be positive in the glassy zone and negative in flow zone like that for the other higher-M samples. Since the negative birefringence at low frequencies could be attributed to the chain orientation, the present result indicated that for the case of birefringence the polymeric modes became dominant at low frequencies even for the lowest M sample.

The data were analyzed with the modified stress-optical rule: The modulus were separated in two components (R and G components). The G component, which is responsible for the glassy behavior, was found to be independent of M. The R component, for which the ordinary stress-optical rule hold well, could be represented with the spring-bead mode theory except for the lowest molecular weight sample. The limiting modulus for the R component at high frequencies decreased with decreasing molecular weight when M < 2k lower than 2k samples. This result suggested that the main chain orientation in the glassy zone decreased with decreasing chain length, probably due to different orientation of the chain ends.

The time-temperature superposition principle was applicable to each of the R and G components and the shift factors were different from each other. Anomalous temperature dependence of the steady state compliance for low M polymers as Plazek reported could be attributed to difference in temperature dependence of the two components.

Wednesday 5:30 Main Foyer PO16

CHARACTERIZATION OF SLIP MECHANISMS BETWEEN CROSSLINKED POLYDIMETHYLSILOXANE AND SILICA SURFACES

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Slip along the die wall has been implicated in the onset of sharkskin phenomena; the objective of this study was to develop understanding of mechanisms governing slip. Quantitative friction stress data were obtained by sliding flat-tipped styli having various known dimensions (less than 95x95 um) and roughness less than 5 nm over a crosslinked polydimethylsiloxane (x-PDMS) substrate. A first set of styli had a native silica (SiO) surface; by using a crosslinked substrate the mechanism of slip was restricted to debonding between the substrate and the SiO surface. A second set of styli was functionalized with linear hydroxyl-terminated polydimethylsiloxane (PDMS-OH) polymers in order to allow slip to occur via a mechanism of disentanglement of the bound PDMS-OH from the crosslinked substrate.

In the limit of low applied normal stress and low velocity, the friction stress on a SiO stylus sliding over the substrate was a factor of ten greater than the stress on a PDMS-OH functionalized stylus. A stronger dependence of friction stress on sliding velocity was observed with a SiO stylus than with a PDMS-OH functionalized stylus. The friction stress versus velocity and normal stress data were fit for each stylus/substrate system with an Eyring model; the activation energy term was about twice as great for the SiO/substrate system than for the PDMS-OH/substrate system. The friction stress for sliding of the PDMS-OH stylus over the x-PDMS substrate was similar to the critical wall shear stress of 4×10^4 Pa noted for sharkskinning of a PDMS melt extruded from a silica capillary by El Kissi et al. (J. Non-Newt. Fluid Mech. 52 (1994) 249-261). This supports the interpretation that in the El Kissi et al. experiment slip occurred via the mechanism of a first polymer layer, which remained bound to the wall, disentangling from the bulk melt.

Wednesday 5:30 Main Foyer PO17

ELIMINATION OF SHARKSKIN AND STRESS REDUCTION USING A BRASS DIE

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We have extruded a linear low-density polyethylene through identical capillary dies fabricated from stainless steel and brass. We confirm a result first reported by Ramamurthy [1]: following an initial transient, sharkskin is not observed on extrudates from the brass die over most of the range of throughputs where sharkskin is always observed with the stainless steel die. We also find that the shear stress is reduced in the brass die relative to the stainless steel die at throughputs in the range where sharkskin is observed with the latter. Finally, the large pressure oscillations observed in the "slip- stick" region with stainless steel are absent with brass, where the transition to the "upper branch" of the flow curve is more gradual.

1. A. V. Ramamurthy, J. Rheol., 30, 337 (1986)

Wednesday 5:30 Main Foyer PO18

THE SPURT PHENOMENON FOR SINGLE INTEGRAL CONSTITUTIVE EQUATIONS

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The spurt phenomenon exhibited by high molecular weight, nearly mono-disperse polymer melts and solutions will be analyzed for single integral constitutive models. The integral form of the Johnson-Segalman model, and a variety of K-BKZ models will be investigated for pressure and wall driven simple shear flows. Asymptotic and numerical results will be presented for the pressure gradient and flow rate controlled cases. The features of the memory kernels and strain damping functions which produce sustained oscillations in the flow rate controlled case will be delineated. The wall driven flows are shown to be linearly unstable along the downward sloping portion of the steady shear stress vs. shear rate curve. We find however that the growth rates are significantly over-predicted, and that there is in fact a significant latent period of time before the unstable solution actually evolves into a layered solution with shear rate discontinuities. Such features could result in misinterpretation of experimental results for high Mw, narrow MWD polymer melts and solutions in parallel plate rheometers.

Wednesday 5:30 Main Foyer PO19

SURFACE INSTABILITIES IN COMPRESSED OR BENT RUBBER BLOCKS

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Biot [1] determined the critical strains at which surface instabilities appear in large blocks (half-spaces) of a neo-Hookean material subjected to different degrees of compression in two directions. Three special cases are: simple compression; compression in one direction with the perpendicular direction constrained; and equibiaxial compression. In each case a surface instability is predicted to occur at a moderate compressive strain, between 33 and 55 %. When a thick elastic block is bent, compression occurs in one direction along the inner surface while the perpendicular direction is held virtually unchanged. Thus, a surface instability would be expected when the surface compression is 44 %. Observations on bent rubber blocks are compared with this prediction. Sharp creases appeared suddenly on the inner surface at a critical degree of bending. However, the critical compressive strain was only about 35 % and the bending curvature was only about one-half as severe as that at which surface instability would be expected.

Rubber articles are often subjected to severe bending but the occurrence of sharp creases on the inner surface could well pass undetected. Nevertheless, they would be potential failure sites. Also, moving creases ("Schallamach waves") appear in a rubber surface underneath a frictional slider [2] and may play a role in rubber abrasion. Further elucidation of the critical conditions is needed.

REFERENCES
1. M. A. Biot, "Mechanics of Incremental Deformations", Wiley, New York, 1965.
2. A. Schallamach, Wear 17, 301 (1971).

Wednesday 5:30 Main Foyer PO20

SURFACE ROUGHNESS OF DOUGH DURING EXTRUSION

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Smooth balls of dough emerge as rough surfaced strands upon extrusion through a die, while the throughput rate fluctuates even when the pressure is held constant. The degree of roughness of the strands as well as the fluctuations in throughput rate decreased as doughs were mixed for longer periods of time. Bagley et al. first reported the above observations as little understood flow anomalies in dough extrusion. In this study we show that the same behaviors are also observed in constant pressure dough extrusion and that the surface defects observed for dough are different from those of polymer shark-skin phenomena as reported for polymer melt extrusion. Combination of scanning electron micrograph information of the dough strands along with the shear rate effects on the extrusion pressure profiles point to an ever-present stick-slip flow, possibly arising from dough - die surface interactions. Our results indicate that the scale of the stick and the slip during extrusion decreases as more and more starch granules are covered by the flour proteins during mixing.

Wednesday 5:30 Main Foyer PO21

SOME RHEOLOGICAL PROPERTIES OF HUMAN VOCAL FOLD TISSUES

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Using a parallel-plate rotational rheometer, small- amplitude oscillatory shear experiments were performed to quantify the rheological properties of human vocal fold mucosal tissues (the epithelium and the superficial layer of the vocal fold lamina propria) as a function of frequency (0.01Hz to 15Hz). Implantable biomaterials currently or potentially useful in the surgical treatment of vocal fold defects were also measured (Teflon, gelatin, collagen, fat, hyaluronic acid, and fibronectin). Results showed that intersubject differences as large as an order of magnitude were often observed for the shear properties of vocal fold mucosa, part of which may be age- and gender- related. Shear properties of some surgical biomaterials (Teflon, gelatin, collagen) were quite different from those of vocal fold tissues, while for others they were much closer. Theoretical modeling showed that the shear properties of human vocal fold mucosa may be described by a quasi-linear viscoelastic theory and a statistical network theory, based upon which data extrapolations to frequencies of vocal fold oscillation (on the order of 100Hz) were possible. Implications of the findings for vocal fold augmentation surgery were discussed.

Wednesday 5:30 Main Foyer PO22

RHEOLOGY IN DAILY LIFE – THE NEW ORBITZ DRINK

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In February 1997 the Clearly Canadian Beverage Co. introduced a new soft drink to the world – ORBITZ. The new drink consisted of a clear liquid with colorful gel beads "suspended" in the fluid. It was claimed that the colored beads were gels consisting primarily of liquid (true) and that the beads remained suspended in the clear fluid because they were neutrally buoyant – having the same density as the suspending liquid. It was also claimed that adding alcohol to the drink would cause the gel beads to sink in the clear liquid. Within seconds of visual inspection of the flow properties of the gel beads in the clear outside liquid of the ORBITZ drink it was obvious to the "trained rheological eye" that there was more at work in this drink than just gravity – there was viscoelasticity! The listed ingredients in the ORBITZ drink included Gellan Gum and Xanthan Gum. The gel beads were separated from the clear suspending liquid (orbitz fluid). The density of the orbitz fluid and beads were measured and then simple tests were made to examine the neutral buoyancy explanation. All buoyancy tests were done using the actual gel beads from the ORBITZ drink. With the addition of water or alcohol to the orbitz fluid, the fluid density could be both lowered and raised, with no change in the ability of the orbitz fluid to suspend the gel beads. Thus, the neutral buoyancy explanation alone does "not hold water"! Rheological tests on the orbitz fluid were performed using the Bohlin CS-50 rheometer. As expected from the visual observations, the orbitz fluid was determined to be "weakly viscoelastic". However, a surprising result was obtained which basically provided the key concept for the explanation of the ability of the orbitz fluid to suspend the gel beads. This result, along with attempts to reproduce the orbitz fluid in the laboratory, will be presented at the SOR poster session.

Wednesday 5:30 Main Foyer PO23

DYNAMICS OF STRUCTURE FORMATION IN HIGHLY-FILLED ORGANO-CERAMIC COMPOSITES

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Reactive organo-ceramic composites, consisting of calcium aluminate cements embedded in a dense polymer matrix, represent an important new class of high-strength materials. These systems have the advantage that they can be fabricated at or near room temperature as extrudable pastes prior to heat treating to produce high strength products. The paste state is generated by chemical and/or physical-chemical interactions that take place between the organic and ceramic phases during high shear mixing, leading to rheological properties similar to those of highly filled polymer melts. In recent studies [1,2] we have shown that torque rheometry in Banbury mixing can be used to monitor the evolution of the mixing mechano-chemistry and associated paste stiffening in such systems. In order to more quantitatively describe the interactions that take place during mixing, we have measured the kinetics of structure formation in four different model systems which show stiffening due to the following mechanisms: 1) polymerization of the organic phase, 2) crosslinking of the organic phase, 3) flocculation of the ceramic phase particles, and 4) linking, either chemically or physically, of the ceramic phase particles to the organic phase molecules. Continuum analyses of these systems are based on non-linear generalizations of viscoelastic (spring-dashpot-slider) models for highly filled systems, similar to the approach used by White [3]. Data for the time/stress history evolution of structuring can be modeled in terms of a time-dependent modulus that follows a kinetic equation. Predictions of the stress and torque behavior for several deformation kinematic histories will be presented.

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2. J.A. Walberer and A.J. McHugh, Advn. Cem. Bas. Mat., in press (1998).
3. J.L. White, J. Non-Newtonian Fluid Mech., 5, 177, (1979).

Wednesday 5:30 Main Foyer PO24

DYNAMIC RHEOLOGICAL PROPERTIES OF HDPE/ETHYLENE-ALPHA-OLEFIN COPOLYMER BLENDS

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The objetive of the present work is to obtain rheological evidences of blend miscibility in blends of polyethylenes of different branch contents. The following blends were prepared in a wide composition range by twin-screw extrusion: LLDPE/HDPE (where two different HDPE were used, one was a highly linear inyection molding grade and the other an extrusion grade 1-butene copolymer with a bimodal distribution of molecualr weights) and VLDPE/HDPE (where two different VLDPE were employed, one was obtained by modified Ziegler-Natta catalytic system and the other by metallocene catalysis). The differences observed in the dynamic rheological properties of the neat resins evidenced their varied structural characteristic, such as short chain branching content and distribution and diverse molecular weight values and molecular weight distribution functions. The dynamic rheological properties of the

blends indicated that in general the LLDPE/HDPE systems seem to be miscible in the melt in a wide composition range. However, the VLDPE/HDPE blends exhibited a certain composition range were the Cole-Cole plots evidenced at least two different relaxation processes. A higher content of branched polyethylene favored melt heterogeneity. Parallel DSC studies of these blends also gathered indirect information that confirmed the possible phase separation of the VLDPE/HDPE blends as well as the miscibility of the LLDPE/HDPE blends.

Wednesday 5:30 Main Foyer PO25

RHEOLOGICAL AND MORPHOLOGICAL ASPECTS OF PHASE TRANSITION IN A POLYMER BLEND

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The phase separation of a blend of moderate-molecular weight polystyrene (PS) and polyvinylmethylether (PVME) has been studied under oscillatory shear in a Rheo-SALS device which combines a rheometer with a small-angle light scattering (SALS) assembly. Simultaneous rheological and morphological studies of this type have not been previously reported on this blend. The PS is a monodisperse polymer of molecular weight 123,000 g/mole. The PVME was fractionated by differential precipitation to obtain fractions with polydispersities of approximately 1.3. A PVME fraction with a molecular weight of 73,000 g/mole was chosen for these experiments. The blend displays a temperature-dependent low-frequency plateau in G' in the two-phase region. The shift factor can be used as an indicator of the phase transition, as a divergence from the WLF equation is seen in the two-phase region. Rheo-SALS results documenting the morphological changes accompanying the rheometric transitions will also be presented.

Wednesday 5:30 Main Foyer PO26

NONEQUILIBRIUM THERMODYNAMICS MODELING OF CONSTITUTIVE EQUATIONS FOR POLYMER BLENDS AND COLLOIDS BY GENERIC

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The model of Doi and Ohta for multiphase flow is developed and analyzed from a thermodynamic perspective using the GENERIC {General Equation for the Non-Equilibrium Reversible Irreversible Coupling} formalism. A procedure for obtaining a set of "thermodynamically consistent" transport equations is illustrated. Generalizations of the model of Doi and Ohta to stable droplet dispersions and entropically governed droplets are performed. The results demonstrate that the modified Doi-Ohta model is thermodynamically consistent, and is thus a valid set of transport equations for multiphase flow. Steady state results are compared against "exact" simulation results to assess the model's accuracy.

To model dispersions of colloidal particles, the Smoluchowski equation is analyzed within the GENERIC framework. A stress tensor is derived in terms of the particle microstructure and colloidal interactions that is thermodynamically consistent with the microstructure equation. Results for the pair-correlation level demonstrate the importance of maintaining thermodynamic consistency when predicting rheological properties from particle interactions.

These derivations and illustrated results demonstrate the how the GENERIC formalism can improve the theoretical basis of models and constitutive equations for transport in complex fluids.

Wednesday 5:30 Main Foyer PO27

SHORT-TIME DYNAMICS OF CONCENTRATED CHARGE STABILIZED POLYMER DISPERSIONS

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For this study, well characterized monodisperse polymer dispersions of different diameters (310, 200, 120nm) were used. The highly charged dispersions were cleaned thoroughly and the interaction potential was influenced by variation of the salt content from 0.1mM KCl to 50mM KCl. Rheological properties in the high frequency limit were determined by a surface loaded torsional resonator. High-frequency modulus and high-frequency viscosity could be extracted from the data obtained from the resonator operating at a frequency of ca. 8kHz. A controlled stress rheometer was used to measure the elastic shear modulus at frequencies up to 50 Hz. Zero-shear viscosity was measured by a controlled strain rheometer. As expected zero-shear viscosities showed a strong dependence on the salt and the viscosity diverges clearly below a volume fraction of 0.61 commonly found for monodisperse hard sphere like dispersions. Results for the high frequency viscosity are compared to the short-time self diffusion coefficient determined by means of fibre-optic QELS. For the high frequency viscosity and the short-time self diffusion we found, that both quantities are insensitive to the direct interparticle interactions. Quantitative agreement between the experimental results and micromechanical hard sphere theory is observed for a range of particle sizes and added salt content. However, while the reciprocal of the short-time delf diffusion coefficient shows a similar concentration dependence as the high-frequency viscosity, the two do not obey a generalized Stokes-Einstein relation. High-frequency moduli were used to calculate effective surface charges according to a model recently presented by Bergenholtz. The calculated surface charges are compared to surface potentials obtained from electrophoretic mobilities. Buscall's model for calculating the surface potential from the plateau moduli at low frequencies was used to acquire additional data for comparison.

Wednesday 5:30 Main Foyer PO28

MEASUREMENTS AND MODELING ON A COLLOIDAL DISPERSION OF POLYMERICALLY STABILIZED SPHERES

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Rheological measurements have been done on the relatively new system of silica particles with end-grafted PolyDiMethylSiloxane (PDMS) surface-chains dispersed in heptane. The polymer chains form a brush-like structure with a brush height comparable to the silica core radius

Both harmonic oscillatory and steady shear measurements were performed at different concentrations giving the elastic modulus at low and high frequency and the viscosity at both low and high shear rate. At a certain volume fraction ϕ_m the low shear viscosity diverges and above ϕ_m the low frequency storage modulus becomes nonzero. This marks a transition from liquid-like to solid-like behavior. Below ϕ_m the behavior of the dispersion resembles that of hard spheres in which the polymer layer is part of the hard sphere.

The high shear viscosity can be described with a modified version of the model of Potanin and Russel (Phys. Rev. E. 52:730 1995). In this modeling it is assumed that the lubrication force is the dominating contribution to the viscosity. The polymer layer is described as a porous medium using Brinkman's equations. We changed the model by improving the boundary conditions which resulted in a good fit with the experimental data.

The storage modulus G' at high frequency is modeled using the work of Elliott and Russel (J. Rheology 42:361 1998). This model can be used for calculating G' in the full range of volume fractions since both inter-particle forces and hydrodynamic forces are included as well as the radial distribution function calculated from Monte Carlo simulations. The inter-particle forces reflect the deformability of the polymer layer. We use a description for the inter-particle force in which curvature of the polymer layer has been taken into account. The values of G' calculated with our description of the inter-particle force, are in agreement with the experimental data.

Wednesday 5:30 Main Foyer PO29

MICROSTRUCTURE AND RHEOLOGICAL PROPERTIES OF AQUEOUS CTAB SOLUTIONS IN THE PRESENCE OF SODIUM SALICYLATE

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We considered the effects of sodium salicylate (NaSal) on the rheological and optical properties of aqueous cetyltrimethylammonium bromide (CTAB) solutions. The CTAB concentration was fixed at either 0.005M or 0.05M, both of which were far above its critical micelle concentration, and the molar ratio, [NaSal]/[CTAB], was varied from 0.1 to 10. The experimental result showed that rheological responses of the present surfactant solution were influenced strongly by concentrations of the constituent substances and temperature. Specifically, 0.005M CTAB solution that underwent shear thinning at low shear rates exhibited shear thickening at high shear rates for the molar ratio ranging from 0.5 to 3.0. In some cases, the solution experienced shear thinning again at even higher shear rates. The observed rheological behaviors were clearly due to the flow-induced microstructure evolution in the solution. Meanwhile, for 0.05M CTAB solution, the onset of shear thickening was not observed and instead the stress plateau appeared at a moderate shear rate.

For the low molar ratio below 0.3, the surfactant solutions behaved like a Newtonian fluid. However, as the molar ratio increased, the deviation from Newtonian behaviors became pronounced and the nonlinear viscoelasticity and relaxation behaviors were distinctively observed. For illustrative purpose, the viscoelastic behaviors were correlated by the Maxwell relaxation model. The relaxation behavior was strongly dependent on the molar ratio, which was also confirmed by the rheo-optical observation. Further, optical intensity fluctuation as a function of the shear rate was consistent with the phase transitions predicted from the rheological responses.

Wednesday 5:30 Main Foyer PO30

EFFECT OF TUBE DIAMETER ON VISCOSITY MEASUREMENTS FOR SURFACTANT SOLUTIONS

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An adequate knowledge of the solution viscosity is essential when one conducts experiments with surfactant solutions, not only to characterize the fluid from a fundamental rheological point of view, but also when one deals with macroscopic flow such as in Drag Reduction studies, for example. Indeed, in the latter case, the use of an appropriate viscosity is critical to the analysis and understanding of the data. In our work, we have conducted experiments where we measured the viscosity of various surfactant solutions through laminar flow in tubes covering a wide range of diameters. It was observed that some of these fluids led to viscosity measurements which depended strongly on the tube diameter, whereas others did not. This laminar diameter effect is likely related to a similar effect observed previously in concentric cylinder rheometers where the gap was also found to affect profoundly the measurements. This effect is thought to be linked to the formation of a shear-induced structure phase in the fluid. Some data on this laminar diameter effect and interpretations of the findings will be presented.

Wednesday 5:30 Main Foyer PO31

DYNAMICS OF MICELLAR STRUCTURE FORMATION AND BREAK-UP IN TURBULENT FLOW OF SURFACTANT SOLUTIONS

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The shear stresses generated in turbulent flow of drag-reducing surfactant solutions have a complex effect on the micellar structures present in the flow. For instance, a minimum level of shear stress must be exceeded for large-scale shear-induced structures (SIS) -widely believed to be necessary for the apparition of the drag reduction phenomenon- to be present. On the other hand, if a critical shear stress is exceeded, the micelles or micellar structures begin to break down and the drag reduction level begins to decrease. This breakdown is reversible, however, unlike the permanent mechanical degradation of polymeric solutions. We have studied the dynamics of the breakdown and regeneration of the micelles and micellar structures for a number of fluids and flow conditions. In particular, the effect of temperature and concentration on those processes were investigated and compared to data available in the literature on micellar dynamics for still fluids - typically from temperature and pressure jumps experiments. We have also observed interesting instability phenomena during recovery of shear-degraded micelles. These various results on the breakdown and recovery of micelles are not only critical to the successful implementation of drag-reducing fluids in industrial applications, but may also -when compared to micellar dynamic theories for still fluids- shed new light on the fundamental physics of the dynamics of micellar systems.

Wednesday 5:30 Main Foyer PO32

TURBULENT PIPE FLOW DRAG REDUCTION WITH NARROW DISTRIBUTION POLYSTYRENE MATERIALS- A TEST OF DRAG REDUCTION THEORIES

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Drag reduction caused by dilute solutions of monodisperse, high-molecular weight polystyrene materials (TosoHaas) under turbulent flow conditions in a single-pass pipe flow apparatus was investigated. The effects of polymer molecular weight and concentration on the "onset" and the magnitude of the drag reduction (%DR)were examined for very dilute polymer solutions. Shear degradation studies were also carried out to elucidate the extent and effects of the drag reduction for very high molecular weight polymers. Blends of high molecular weight, narrow distribution polystyrene samples were studied as model systems to examine molecular weight distribution effects. In particular, the presence of a small amount of a high molecular weight tail on both the onset and %DR were studies. The results indicate the following: · "Onset" is controlled by polymer molecular weight, with little or no effect of polymer concentration. · Polymer concentration affects the %DR. · The Virk's MDA can be reached only with very high molecular weight polystyrene sample (MW = 20000000). · In blends of monodisperse polymers, the highest molecular weight component determines the onset and dominates the %DR. · Shear degradation not an issue for most polymers, particularly when determines the onset point. · Shear degradation does occur for repeated passes through the system at high Re. It is expected that the highest molecular weight materials are most effected. The "Yo-Yo" model time-scale based theory proposed by Ryskin was examined, and several deficiencies were found. In addition, it was found that when time-scale theories are used to predict the onset point, the shear rate along the vortex line of the turbulent eddies is more appropriate to be used than the wall shear rate. Using this quantity and the maximum polymer relaxation time from dilute solution theory, De = 1-2.5 were calculated at the onset point.

Wednesday 5:30 Main Foyer PO33

RHEO-OPTICAL STUDY OF ASSOCIATIVE POLYMER SOLUTIONS

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Flow birefringence and dichroism of classical hydrophobically either end-capped or grafted polymers have been studied. Different concentrations in the vicinity of c* have been investigated. Both steady state and transient experiments have been considered. Comparison between the two types of polymers shows that the relaxation of end-capped chains is essentially due to the life time of an end-group inside an hydrophobic aggregate, especially for rather low molecular weight polymers. This process is well described by a single relaxation time. On the other hand, when hydrophobic groups are randomly located along the chain backbone, the relaxation is better described by a power-law. In this latter case, start-up experiments show a very pronounced overshoot in birefringence, as it is commonly encountered in concentrated polymer solutions. This overshoot will be characterized as a function of concentration and shear rate. A comparison with classical concentrated polymer solutions will be presented.

Wednesday 5:30 Main Foyer PO34

RHEO-OPTICAL BEHAVIOR OF POLY-L-LYSINE

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The synthetic polypeptide, poly-L-lysine represents an interesting system for study since the macromolecule can exist in a variety of conformations in aqueous solution, depending on temperature, pH and salt concentration. Biological functions of numerous proteins are closely related to their conformational states, and therefore an understanding of how flow affects them can be important. Earlier work[1] using laser-Raman spectra suggests that shear flow enhances hydrophobic interactions and hence favors the alpha-helix to beta-sheet transformation. In this work, we use flow-birefringence as a tool to study the effect of simple shear on the random coil to alpha-helix transition. The birefringence of poly-L-lysine in the helical state is 1 to 2 orders of magnitude greater than that in the coiled state, thus giving an indication of its conformation. Under quiescent conditions, aqueous poly-L-lysine exists as a random coil, but transforms into a helix with the addition of methanol, the critical methanol concentration being 87%(vol).In this work we have studied the effect of shear rate on the transient and steady birefringence of poly-L-lysine in methanol-water solutions of varying methanol content in the region of the helix-coil transition. Transient overshoots and relaxation times following shear deformation allow quantitative insights on the effects of molecular rigidification produced by the conformational transitions. Our work indicates that simple shear flow enhances the coil-helix transition. Interpretation of these data in terms of a molecular bead-spring model for semi-flexible behavior (i.e one in which adjacent beads exhibit a resistance to bending as well as stretching deformations) will be presented.

Reference: 1. Biopolymer, Vol. 45, 239-246(1998)

Wednesday 5:30 Main Foyer PO35

THE RHEOLOGY OF DENDRIMERIC AND HYPER BRANCHED POLYMERS

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Results of some of the studies of the role of molecular variables on the rheology and viscoelastic behavior of hyper branched (HBP) and dendrimeric systems being carried out in our laboratory will be presented. Polyether-imide-based HBPs of various molecular weight and end-group functionality have been synthesized in our laboratories and are being compared with the behavior of commercially available dendrimeric systems. Measurements include standard dilute solution capillary viscometry, steady and oscillatory shear stress-shear rate measurements, and relaxation following step shear strains. Comparisons of HBPs and their linear analogs as functions of temperature and concentration will be shown. While dendrimeric molecules having precise architectures exhibit simple Newtonian behavior, our HBPs exhibit significant shear thinning as well as pronounced viscoelastic characteristics depending on the system molecular weight and concentration. These results suggest the likelihood of entanglement-based dynamics.

Wednesday 5:30 Main Foyer PO36

VISCOELASTICITY OF TIGHTLY-ENTANGLED SOLUTIONS OF SEMI-FLEXIBLE POLYMERS

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A molecular model has been developed to describe the viscoelastic behavior of concentrated isotropic solutions of semi-flexible (i.e., worm-like) chains. A key elementin this model is the derivation of a microscopic expression for the intramolecular contributions to the stress in a solution of worm-like chains, which may be expressed as a sum of contributions arising from: i) deformation of the distribution of chain curvatures (curvature stress), ii) anisotropy in the distribution of the orientations of chain ends (orientation stress), and iii) forces exerted tangentially along the chain (tension stress). Motivated in part by recent studies of solutions of actin protein filaments, a generalized reptation model has been constructed to describe a "tightly-entangled" regime in which the persistence length greatly exceeds the tube diameter. The predicted low-frequency complex modulus of uncrosslinked solutions of long, tightly-entangled chains is dominated by the curvature stress, which decays by reptation, and yields a broad elastic plateau. The predicted plateau modulus of a lightly-crosslinked gel or transient network is much larger than that found for uncrosslinked solutions, and is instead dominated by the tension stress. The predicted high-frequency response is always dominated by the tension stress, which yields a generic frequency dependence of $G^*(\omega) \sim \omega^{3/4}$ for the complex modulus, as observed in several studies of actin solutions. The response to large amplitude step deformations of mobile chains is predicted to be strain thinning, though less drastically so than in entangled fluids of flexible polymers.

Wednesday 5:30 Main Foyer PO37

RHEOLOGICAL BEHAVIOR OF ELECTRORHEOLOGICAL FLUIDS: EFFECT OF THE DIELECTRIC PROPERTIES OF LIQUID PHASE

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Electrorheological (ER) fluids composed of non-colloidal silica gel particles of irregular shape and liquids with different dielectric properties are studied in this work. The rheological behavior of the suspensions is analized in the diluted and semiconcentrated regimes under different constant electric fields. Initially, the dielectric properties and conductivity of the liquids and suspensions are studied with particular attention to the dependence of the dielectric relaxation times on particle concentration and their relation with the conductive behavior. Rheological tests under applied electric fields elucidated the dependence of the yield stress on the intensity of the electric field and the ratio of the dielectric properties of the solid and liquid phases. It was found that the yield stress scales as $(\phi E^2)^\alpha$, where E is the electric field, ϕ is the particle volume concentration and α is a constant which depends on the spatial arrangement of the particles. When the particle concentration is the highest in the liquid with the largest dielectric constant, an electronegative effect is observed, presumably due to the electrophoresis phenomena.

Wednesday 5:30 Main Foyer PO38

MACROSCOPIC APPROACHES TO ER AND MR VIA ELECTRO- AND MAGNETOSTRICTION

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We will demonstrate an effective macroscopic approach to modeling ER and MR suspensions derived from basic thermodynamic principles. Calculation of field-induced stresses reduces to a description of the strain dependence of suspension polarization and magnetization in ER and MR suspensions, respectively. Macroscopic properties of the suspension are described by the same set of material parameters as electro- and magnetostrictive stresses in solids: the dielectric constant ε or permeability μ, and derivatives of the polarization (magnetization) with respect to shear deformation, a_1, with respect to volume deformation, a_2, and with respect to deformation in the field direction, a_3. The first three parameters exist for any isotropic material, and the fourth parameter, a_3, accounts for the field-induced anisotropy. We will discuss experimental methods for measuring these parameters, a microscopic model for predicting these parameters, and compare the model predictions with experimental data.

We will also discuss experimental observations that illustrate how electric and magnetic fields can alter the Young's moduli of polarizable or magnetizable elastic materials. Such phenomena can also be interpreted via the thermodynamic approach described above. The magnetoelastic or electroelastic response is stronger for materials with lower Young's moduli; thus elastomeric composites with polarizable or magnetizable inclusions are among the most interesting materials for practical applications. We will present a macroscopic model describing electro- and magnetoelastic phenomena in composite materials, as well as experimental techniques and a microscopic theory for evaluation of material parameters introduced by the macroscopic model. We will also consider deformation of materials in applied fields for several example configurations that permit rigorous analytical analysis.

Wednesday 5:30 Main Foyer PO39

POLARIMETRY AND SALS EXPERIMENTS TO CHARACTERIZE FERROFLUIDS SUBJECT TO AN EXTERNAL MAGNETIC FIELD

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We have characterized the aggregation process of ferrofluids when a magnetic field is applied using two optical techniques: small angle light scattering (SALS) and polarimetry.

The measurements were carried out using two different magnetic fields: an alterning magnetic field (on-off) along a fixed axis and a rotating magnetic field, both in the direction perpendicular to the laser beam.

Using the scattered light patterns obtained by SALS technique we studied the evolution of suspension structure as a function of the strength of the applied field and the particle volume fraction. We analized the structural anisotropy in the sample by means of birefringence and dichroism experiments.

In order to interpret our measurements, we have derived a theoretical model which takes into account the behavior of a magnetic particle in a fluid in presence of a magnetic field. This model agrees with our experimental results.

To conclude, we point out the importance of the rotating magnetic field case, because this technique will allow us to measure the viscosity at high shear rates of the solvent.

Wednesday 5:30 Main Foyer PO40

RHEOLOGICAL PROPERTIES OF PHYSICAL NETWORKS FORMED IN LIPOPOLYMER MONOLAYERS

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Phospholipid bilayers supported on solid substrates have considerable interest as models for investigating cell membranes. With a model cell membrane a better understanding of the cell recognition process and the influence of proteins can be achieved, which can be utilized in engineering biosensors. To fabricate these supported bilayers, it is required to have the bilayer decoupled from the substrate to avoid limiting the lateral mobility of macromolecules in the membrane. This separation is achieved by introducing a polymer cushion between the phospholipid bilayer and the support. A viable method to create this polymer cushion is to incorporate lipid molecules tethered to polymer chains (lipopolymers) into the phospholipid membrane.

In this work we investigated monolayers of a phospholipid attached to a poly (ethylene glycol) chain at the air-water interface using a Langmuir trough. By varying the surface concentration of the lipopolymer, different conformations of the submerged polymer chain can be achieved: pancake at low densities, mushroom at intermediate densities, and brush at high densities. By measuring the mechanical shear properties with an interfacial stress rheometer we were able to detect the onset of a physical network in the brush conformation. At low and intermediate densities the poly (ethylene glycol) chain is hydrated with water molecules. When the brush conformation is achieved, some of the water is squeezed out to accommodate a higher packing density. As the water is removed, it creates vacant H-bonding sites which can bind to water molecules attached on adjacent chains. Water acts as an intercalating agent to create a physically cross-linked monolayer. We detect the cross-linking by observing a step increase in the surface storage modulus, G_s'. The onset of the formation of the physical network can be altered by changing the H-bonding sites (by changing the pH) or by changing the H-bonding strength (using D_2O for a subphase).

Wednesday 5:30 Main Foyer PO41

VISCOELASTIC BEHAVIOR OF POLYMERS TETHERED TO THE AIR/WATER INTERFACE

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We present here an new experimental approach to get more insights into the dynamics of polymer chains tethered by one end to an interface. We investigate the linear viscoelastic behavior of solvent-free polymer brushes as monolayers at the air/water interface, depending on the surface concentration and chain length. These brush-like monolayers, obtained by spreading hydrophobic polymers with a hydrophilic head group onto the water surface, are typically 20-50 nm thick. The tethering density can be easily varied by lateral compression of the film with the movable barrier of a Langmuir trough. Their linear viscoelastic properties, e.g. dynamic shear moduli versus frequency, are analyzed directly at the air /water interface, by the technique of interfacial shear rheology. The shear plane being parallel to the interface, within which the chain ends are able to move, this method provides a very interesting way to evidence topological constraints, like entanglements and probe the influence of chain anisotropy. We will present our results obtained on polyisoprene chains terminated by a sulfonated head group with different molecular weights covering a range below and above the critical molecular weight of bulk polyisoprene.

Wednesday 5:30 Main Foyer PO42

DNA MICRO-HYDRODYNAMICS: A TOOL IN OPTICAL GENE MAPPING

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One of the major drawbacks impeding the pace of ongoing gene sequencing research is the inability of the state-of-the-art technology to read long DNA fragments quickly. This work analyzes a novel technique developed by Schwartz and co-workers[1] to circumvent this problem. The idea is to stretch long DNA segments on a flat surface, thereby making them more amenable to subsequent analysis using digestion by restriction enzymes and measurement of the resulting fragment lengths. The commonly observed phenomenon of drying droplets is put to use for this purpose[2]. The radial fluid flows that are generated in the process help unravel the coiled DNA molecule. The current focus is to describe the mechanics of DNA stretching on a micro-scale by means of Brownian Dynamics computer simulations[3]. Statistical Analysis is performed on the efficiency of stretching induced by this flow. Preliminary results are shown here.

References:
1. Jing et al., PNAS 95:8046, 1998
2. Deegan et al., Nature 389:827, 1997
3. Larson et al., Phys Rev E 55:1794, 1997

Wednesday 5:30 Main Foyer PO43

FLUID MECHANICAL STUDIES OF THE EFFECTS OF POLYMER CONCENTRATION IN THE BOGER FLUID REGIME

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A large number of studies of the flow behavior of dilute polymer solutions of the so-called Boger fluid type have led to the conclusion that these materials can be modeled relatively successfully for extension-dominated flows via the dumbbell-based Chilcott-Rallison constitutive model, though generally with values of the extensibility parameter L that are significantly smaller than would be estimated from the polymer molecular weight. This reduction in L is a consequence of polymer interactions enhanced by the flow-induced deformation of the polymer. In the present work, we examine the optimal choice of L for polystyrene solutions at concentrations $c/c^* \sim O(1)$. We show that the Chilcott-Rallison model gives very good predictions for both the polymer chain configuration (as measured via birefringence) and also for the velocity field (as measured via dynamic light scattering) at the stagnation point of a two-roll mill which is started from rest, provided that L is chosen to match the asymptotic large strain rate birefringence in a steady extension-dominated flow.

Wednesday 5:30 Main Foyer PO44

A BROWNIAN DYNAMICS STUDY OF SOLVENT QUALITY EFFECTS ON POLYMER IN EXPONENTIAL SHEAR FLOW

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It has been well established that free polymer in solution can take on dramatically different equilibrium configurations depending on the quality of the surrounding solvent. Furthermore, solvent quality also plays a pivotal role in determining the unraveling process and subsequently the rheological properties of polymer in a uniaxial extensional flow.(Kwan and Shaqfeh, 1997). In the present study, we use Brownian dynamics simulation to investigate the behavior of a polymer in an exponential shear flow which is defined as 'strong' if one considers the configuration and stress of Hookean dumbbells. This flow is also interesting since it can be readily created in the laboratory and therefore has the potential for allowing the extensional characteristics of rheology to be examined without relatively sophisticated equipment. In an exponential shear flow the shear rate varies exponentially with time, and it was proposed by Doshi and Dealy (1987) that this flow had the potential for creating large configuration change in polymer molecules. In our study, the transient startup and subsequent relaxation after flow of non-interacting polymer chains were simulated over a wide range of shear and shear-ramping rates. We find that indeed exponential shear is able to produce considerable polymer stretch within a finite strain, and furthermore, there exists a stress-birefringence hysteresis that was previously observed in uniaxial extensional flow. This behavior is studied in both good, theta, and poor solvents. If time permits, we shall also present simulation results on the rheological behavior of polymers in a biaxial extensional flow and compare our results to those of Doyle and Shaqfeh (1996) for a uniaxial extensional flow.

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ONSET AND EVOLUTION OF ELASTIC INSTABILITIES IN FLOW THROUGH PERIODIC ARRAYS OF CYLINDERS

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Viscoelastic flow past periodic arrays of cylinders has been shown to be a good pore model for flow through porous/fibrous media, which finds applications in many fields of science and engineering such as enhanced oil recovery and manufacturing of polymer matrix composites. To date, purely elastic instabilities have been observed experimentally in various flows past periodic arrays of cylinders. Specifically, the mechanisms, the onset and the spatial and temporal characteristics of the secondary flow depend strongly on the geometry i.e., the center to center cylinder spacing, the proximity of solid walls and the geometric arrangement of the cylinders (Skartsis et al. 1992, Chmielewski et al. 1993, McKinley et al. 1993, Byars et al. 1994, Liu 1997, Khomami and Moreno 1997).Recent theoretical analysis of this flow has predicted, for closely spaced periodic array in a channel, the possibility of a 2-d and time dependentshear-mode instability that manifests itself as propagating vortices localized near the solid walls (Sureshkumar et al 1997). However, all of the earlier experimental studies have focused their attention in the wake and/or the surface of the cylinders. Motivated by the wealth of dynamics exhibited by this class of flows. Specifically, in this study the stability and post critical dynamics of flow of well-characterized polymeric solutions (i.e., Boger fluids) through various periodic arrangement of cylinders has been examined through detailed pressure measurements as well as kinematic characterization utilizing Digital Particle Imaging Velocimetry (DPIV). In particular, the onset conditions and the temporal and spatial evolution of secondary flows as a function of pore geometry and fluid elasticity have been examined.

Wednesday 5:30 Main Foyer PO46

COMPUTATIONAL SIMULATIONS FOR PROTEIN STRUCTURE PREDICTIONS

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With the revolution in sequencing technology, the gap between biological sequence information and structural information is widening. New efforts in computational biology that borrow from concepts familiar to polymer rheologists show great promise in addressing this gap. On the algorithmic component of the folding simulation, we examine the Weighted Ensemble Brownian dynamics algorithm, a biased Brownian dynamics scheme that improves the efficiency of free-energy-barrier crossing through the adjustment of probabilistic weight assigned to each Brownian configuration. Using a simplistic four-helix-bundle protein model, the algorithm manages to estimate folding time that is on the order of seconds or longer. An equivalent simulation using unbiased Brownian dynamics would have been impossible due to computer resource limitation. On the force-modeling component, we investigate a novel class of interaction potentials that are derived from the known protein structures. Preliminary results from the comparison of the current and superseded protein structures suggest that the structure-derived potentials can accurately identify native structures of proteins.

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