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Symposium PO
Poster Session

Organizer: Rangaramanujam M. Kannan

Wednesday 5:30 Grand Terrace PO1

RHEOLOGY OF SUSPENSIONS OF NON-BROWNIAN FIBERS WITH ADHESIVE CONTACTS

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An experimental investigation is undertaken into the shear thinning behaviour of non-Brownian rigid fiber suspensions in Newtonian fluids. In particular, we investigate the influence of the shear stress and fiber concentration on the transient and steady shear viscosity of the suspension. The shear stress is adjusted by varying both the shear rate and the solvent viscosity. In the semi-dilute regime (low collision frequency among the fibers), the suspension is found to be nearly Newtonian over the stress range we investigated. In the concentrated regime, the suspension becomes shear thinning below a certain shear rate. The shear thinning effects increase drastically with concentration and decrease with solvent viscosity. Although shear thinning behaviour of fiber suspensions has often been reported in the literature, its physical origins are not well understood. Here, our experiments are interpreted in the framework of formation and breaking of fiber flocs due to the competition between hydrodynamic and colloidal forces. Our interpretation is confirmed by measurements of the adhesive forces between the fibers.

Wednesday 5:30 Grand Terrace PO2

RHEOLOGY AND MICROSTRUCTURE OF SOLIDIFYING SUSPENSIONS

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The apparent viscosity of alloys during globular solidification cannot be modelled by the classical models for isothermal non-interactive spherical particles derived from Einstein's formulation[1]. It has been shown previously[2] that for a given shear stress, the apparent viscosity follows a modified version of Arrhenius' model[3] with a multifying factor C ranging from 4 to 8:

$$\eta = \eta_{liquid}\, e^{2.5\, C}$$

where ϕ is the solid volume fraction and η_{liquid} the viscosity of the remaining liquid.

Micrographs from semisolid rheology experiments[4,5] with different metallic alloys have been analyzed. Firstly, it appears that classical models taking into account a suspension maximum packing fraction[6] cannot explain solidification rheology. Finally it has been observed that the multiplifying factor C in the modified Arrhenius' model is close to the ratio of the volumes of the spheres determined from the largest diameter and the Waddel disk diameter, as found from particle image analysis. The amplitude of 3-D effects on these 2-D images have been assessed.

An empirical methodology for the evaluation of viscosity is proposed. It is based on, both the estimation of liquid phase viscosity and on post test analysis of the crystals morphology.

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[4] P.A. Joly, R. Mehrabian, J. Mater. Sc., 11:1393-1418, 1976
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[6] R.D. Sudduth, J. Applied Polymer Sci., 50: 123-147, 1993

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Wednesday 5:30 Grand Terrace PO3

RHEOLOGY OF HIGHLY CONCENTRATED, BIMODAL DISPERSIONS WITH COLLOIDAL INTERACTIONS

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The relationship between particle size distribution and viscosity of concentrated dispersions is of great industrial importance, since it is the key to get high solids dispersions or suspensions. The problem is treated here experimentally as well as theoretically for the special case of strongly interacting colloidal particles. An empirical model based on a generalized Quemada equation $\eta = \eta^{\#}(1-\phi/\phi_{max})^{-\varepsilon}$ is used to describe η as a function of volume fraction ϕ for mono- as well as multimodal dispersions. The pre-factor $\eta^{\#}$ accounts for the shear rate dependence of η and does not affect the shape of the η vs. ϕ curves. Colloidal interactions do not show up in the maximum packing parameter ϕ_{max}. The experimentally determined ϕ_{max} values agree very well with predictions from an empirical expression for suspensions with arbitrary particle size distribution extracted from a large number of literature data related to non-colloidal hard sphere suspensions. The exponent ε characterizes the interactions among the particles. Starting from a limiting value of 2 for non-interacting either colloidal or non-colloidal particles ε generally increases strongly with decreasing particle size. Therefore, the viscosity of bimodal dispersions varies not only with the size ratio of large to small particles, but also depends on the absolute particle size. Also, the well-known viscosity minimum for bimodal dispersions with volumetric mixing ratios of around 30/70 of small to large particles vanishes if colloidal interactions contribute significantly.

Wednesday 5:30 Grand Terrace PO4

RHEOLOGICAL SIGNATURES OF SOLID-LIQUID TRANSITIONS IN PARTICULATE SUSPENSIONS

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The transition between liquid-like and solid-like behavior is an important property in the processing of many different suspensions. There are many different names for this type of behavior, such as the appearance of a yield stress, a gel point, or a glass transition. Rheological measurements can be used to locate these transitions, however , the relation between the measurements, interparticle forces and microscopic events are yet unclear. One consequence of this lack of understanding is that the dependence of the results on the observation time of the experiments is an issue.

With computer simulations, we are beginning to connect a microscopic interpretation with the experimental techniques. We use two simulation approaches. The first, a nonequilibrium method strains the suspension and measures the stress vs. strain plot to extract the yield stress in the same way as the vane technique measures a yield stress. The second is an equilibrium method that measures the decay of a stress-autocorrelation function to extract a residual stress that corresponds to a static modulus. For a simplified model system, we use both techniques to locate the transition from liquid-like to solid-like behavior.

Wednesday 5:30 Grand Terrace PO5

FLOCCULATION IN FLOWING FIBER SUSPENSIONS

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Non-Brownian, flexible fibers commonly flocculate in flowing suspensions at relatively low concentrations (< 1% by weight). Using particle level simulations, it is found that flocculation in these suspensions can be induced solely by frictional interactions between fibers with irregular equilibrium shapes---no attractive potentials between particles are necessary. We discuss the effects of fiber equilibrium shape, fiber flexibility, interparticle static friction coefficient, and interparticle attractive potential on flocculation. Mechanical features---fiber shape and friction coefficient---are found to dominate flocculation behavior. Aggregates formed through mechanical mechanisms are qualitatively different than those formed by attractive forces. Characteristics of simulated fiber flocs are compared with experimental observations.

Wednesday 5:30 Grand Terrace PO6

INFLUENCE OF SURFACTANT-INDUCED ELASTICITY ON FLUID MOTION AND MIXING IN A CONTINUOUSLY STIRRED TANK

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The drag reduction capability of surfactants has been attributed to their ability to form flow-induced structures. Since this structure formation is reversible, it has been proposed that surfactants can potentially be used for drag reduction applications that involve moving machine parts/particulates. Using digital particle imaging velocimetry (DPIV), we investigate the influence of surfactants on fluid motion and mixing patterns in a baffled cylindrical stirred tank, equipped with a Rushton turbine. Depending on the type of the counter ion, the surfactant concentration and the impeller frequency, we have observed significant qualitative and quantitative changes in the mean flow, root mean square fluctuations, turbulent kinetic energy, and auto-correlation functions. Clear evidence of surfactant-induced flow elasticity was obtained from flow visualization experiments where the impeller motion was abruptly stopped and a relaxation phenomenon was observed. Comparison of average velocity data obtained with a 0.25mM CTAC/4-CB solution with that obtained for water indicates enhanced velocities for a given impeller frequency, displacement of the center and changes in the shape of the vortex associated with the mean flow, and stabilization of the impeller jet. At higher concentrations (0.5mM or above) the stabilization of the jet was much more pronounced. However, the average flow pattern for this concentration is qualitatively different from that observed for the 0.25mM CTAC solution: the DPIV data show a significant reduction of velocity fluctuations and a number of smaller "mixing pockets" reminiscent of chaotic laminar mixing. We will discuss the potential mechanisms that cause such curious effects. Acknowledgements: ACS/PRF; NSF; Prof. M.P. Dudukovic', Chemical Reaction Engineering Laboratory, Washington University.

Wednesday 5:30 Grand Terrace PO7

FLOW VISUALIZATION OF DRAG-REDUCING SURFACTANT SOLUTIONS IN PIPES

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Some recent measurements of velocity profiles in concentric cylinder viscometers for drag-reducing surfactant solutions showed that most of the velocity gradient across the gap was found in narrow regions close to the walls, with the rest of the fluid moving as a quasi-solid plug. These results also led to the important conclusion that measurements of viscosity in rotational rheometers must be carefully interpreted to avoid misleading estimates, especially when used for drag reduction data analysis purposes. To investigate this issue further we have conducted a number of particle-based and direct flow visualization experiments in pipe flow for these solutions, both in laminar and turbulent flow and with special attention paid to the transition regime. Particle tracing and visualization experiments allow us to estimate the velocity profiles and to investigate the possibility of plug formation in pipe flow. Some visualization results will be presented for a number of flow conditions.

Wednesday 5:30 Grand Terrace PO8

RHEOLOGY OF CELLULOSE ACETATE IN METHYLENE CHLORIDE/METHANOL SOLUTIONS

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We have developed a technique to characterize the oscillatory shear rheology of concentrated cellulose acetate solutions using a modified Couette geometry where the inner cylinder has been replaced with a vane. A barrier layer of an inert solution is also used to inhibit diffusion of the volatile solvent out of the sample. We present Master Curves of viscosity as a function of frequency, formed by independently varying both temperature, solvent composition, and polymer concentration. We find that the onset of shear thinning is proportional to the reciprocal of the zero-shear viscosity, implying that the longest relaxation time is proportional to the viscosity. The viscosity has an Arrhenius temperature dependence. The viscosity-polymer concentration dependence is complicated, but can be approximated as a power law for concentrations above 12%. Varying the methanol content from 6% to 16% does not alter the general form of these functional dependencies. These results will be discussed in the light of recent theoretical models.

Wednesday 5:30 Grand Terrace PO9

THE SOLUTION PROPERTIES OF POLYELECTROLYTES: A CLASSICAL TREATMENT

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The present investigation examines the dilute solution properties of two polyelectrolytes: potassium-p-polystyrene sulfonate and polymethacrylic acid. The Donnan approximation is used as a model for these systems. The molecular weights of the fractionated samples were evaluated and used to determine the theta conditions. The intrinsic viscosities were used to measure the expansion coefficients as a function of added electrolytes. The agreement with the theory was satisfactory. The activity coefficients for the gegenions in the polyelectrolytes were determined using a dropping potassium amalgam electrode. The conductivity of the potassium-p-polystyrene sulfonate solution was compared with those of potassium benzene sulfonate.

Wednesday 5:30 Grand Terrace PO10

RHEOLOGY OF POLYMERIC SOLUTIONS: SHEAR THINNING

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Current polymer characterization methods include preparation of dilute dilute solutions of a polymer and determination of the value of intrinsic viscosity from which one can calculate the polymer DP using pre-established literature data on a and K values of a semi-empirical Mark-Houwink equation. This method is tedious and often ambiguous; in addition, it generates large volumes of waste solvents, which is undesirable from an environmental viewpoint. This work opens a way for a single-point DP and polydispersity determination of moderately concentrated solutions.

An orientation and/or change in shape of particles or macromolecules in the shear flow causes shear-thinning phenomena; as such, they are a function of the entropy of flow. The ΔS should be proportional to the amount of work or energy applied to the system to achieve desired shear rate as well as to the concentration and molecular weight of a polymer. Torque being a momentum of force and having dimensions of energy is a proxy for energy. It will be shown that:

$$RTLn\ \eta_R = RTLn\ \eta_o - T * \Gamma M^m / \phi^p$$

Where: Γ is the torque, Joule/mole,
ϕ is the volume fraction of a polymer in solution (concentration units can be used in dilute solutions), and
η_o is a zero shear viscosity of a system.

The equation describes published data on shear thinning of polystyrene in non-polar solvents with $R^2 > 0.98$.

Wednesday 5:30 Grand Terrace PO11

STABILITY OF NON-ISOTHERMAL VISCOELASTIC TAYLOR-COUETTE FLOW USING TIME-DEPENDENT SIMULATIONS

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Linear stability analyses of viscoelastic Taylor-Couette flow under isothermal conditions have predicted flow transitions to non-axisymmetric and time-dependent states [Shaqfeh, Annu. Rev. Fluid. Mech., 1996]. Also, non-linear stability analysis has shown that the flow bifurcation is supercritical for axisymmetric disturbances [Avgousti and Beris, Int. J. Num. Meth. Fluids, 1993] and subcritical for the non-axisymmetric ones [Sureshkumar et al., Proc. R. Soc. Lond., 1994]. In contrast, it was reported experimentally that the transition to the secondary flow is axisymmetric corresponding to a stationary state with onset Deborah number an order magnitude lower than those reported theoretically [Baumert and Muller, Phys. of Fluids, 1997]. Recently, Al-Mubaiyedh et al. [70th Annual Meeting of SOR, 1998] showed that energy dissipation by viscous heating in the viscoelastic Taylor-Couette flow has a significant influence on the stability characteristics of the viscoelastic Taylor-Couette flow of an Oldroyd-B liquid. First of all, for experimentally realizable values of Peclet and Brinkman numbers, the onset Deborah number predicted by the non-isothermal linear stability analysis is very close to that reported experimentally. Moreover, the most dangerous disturbance is axisymmetric and stationary. In this study, we have used time-dependent simulations to examine the non-linear stability characteristics, i.e., supercritical vs. subcritical bifurcation, of the non-isothermal Taylor-Couette flow of an Oldroyd-B liquid. The time-dependent simulations are also used to examine the non-linear evolution of the disturbance in the post-critical flow regime. We will also discuss the effect of various important parameters such as inertia, solvent viscosity, gap width, and viscous dissipation on the stability of this flow.

Wednesday 5:30 Grand Terrace PO12

A STOCHASTIC SIMULATION APPROACH TO STUDY THE STABILITY AND DYNAMICS OF COMPLEX VISCOELASTIC FLOWS

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Numerical prediction of flow instabilities in viscoelastic flows has attracted a lot of attention among researchers in recent years. Traditionally stability analyses have been performed using spectral techniques, which involve solving generalized eigenvalue problems. However, these methods become intractable when dealing with complex flows due to their prohibitive computational requirements. This problem has been alleviated recently by groups (Sureskumar et al., JNNFM, 82, 57-104; Yang and Khomami, 70th Annual Meeting of SOR) who have used time dependent Finite Element techniques to study the dynamics of complex flows. Despite this, all the aforementioned techniques suffer from an inherent need for a closed form constitutive equation (CE). We illustrate a method of performing stability analyses of viscoelastic flows in non-trivial geometries which does not require the use of a CE. The method has been constructed using a modified form of the concept of 'Brownian Configuration fields' recently introduced by van den Brule et al. (van den Brule et al., JNNFM, 70, 79-101). It involves combining Brownian Dynamics Simulations with time dependent adaptive Finite Element methods (BDS/A-FEM) to study the dynamics of two-dimensional flows. We have demonstrated the feasibility of our technique by studying the stability of a simple flow, namely the Plane Couette Flow (PCF) using the Hookean and FENE dumbbell models. We have compared our Hookean results by performing simulations with its macroscopic counterparts, the Upper Convected Maxwell (UCM) and the Oldroyd-B constitutive equations. Encouraged by the excellent agreement, we have endeavored to apply our technique to a more complex flow like the flow past an array of cylinders. This flow was chosen because its stability and dynamics are well reported in literature. Our results using various dumbbell models and their comparison to the macroscopic results shall be presented.

Paper PO13 has been withdrawn. PO13

Wednesday 5:30 Grand Terrace PO14

LUBRICATED SQUEEZING FLOW OF HERSCHEL-BULKLEY FLUIDS AT CONSTANT FORCE

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Theoretical and experimental studies on squeezing flow of viscous fluids with no-slip or perfect-slip (lubricated) boundary conditions exist in literature. In recent years, more effort is devoted to the analysis of lubricated squeezing flow of viscoplastic fluids. Lubricated squeezing flow (or lubricated compression) technique at constant-speed or at constant-force has become an important tool in food rheology and been utilized over the years to study rheological behavior of various products (e.g., dough, cheese, mayonnaise, peanut butter). Therefore, it is of practical importance to have analytical solutions for viscoplastic fluids in order to evaluate model parameters from squeezing flow data.

In this work, lubricated squeeze flow of a viscoplastic fluid (Herschel-Bulkley) subjected to constant force was analyzed to obtain an expression for sample height as a function of time. The expression obtained for Herschel-Bulkley was verified to reduce, as limiting cases, to those equations previously derived for Newtonian and power-law fluids. Effect of each model parameters (n, K and o) on the response of Herschel-Bulkley fluid in lubricated squeeze flow is examined with selected set of parameter values. The simulation results for Herschel-Bulkley fluid are compared with the behavior of Newtonian and power-law fluids. Moreover, simulated behavior of Herschel-Bulkley fluids is compared with the behavior of mayonnaise in lubricated compression.

Wednesday 5:30 Grand Terrace PO15

PERIODIC MOTION OF PARTICLES SETTLING IN AN AXISYMMETRIC GEOMETRY

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Particle settling in quiescent fluids is important in many industrial processes. Single particle settling in Newtonian fluids has been studied extensively. Less work has been done in non-Newtonian fluids using both single and multiple particles. Two or more particles settling in non-Newtonian fluids exhibit unusual behavior that includes simple interactions to form a coupled group and periodic motion in which the particles preform a complex "dance" as they move through the fluid. This paper reports preliminary results from experiments conducted with groups of three and four particles settling in several different fluids.

Paper PO16 has been withdrawn. PO16

Wednesday 5:30 Grand Terrace PO17

BUCKLING INSTABILITIES IN MODELS OF VISCOELASTIC FREE SURFACE FLOWS

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We study here some theoretical model problems, with the goal of obtaining a better understanding of viscoelastic free surface flows and their unique flow instabilities. The first analysis examines the stability of inward radial flow of an Oldroyd-B fluid in a washer-shaped domain, showing that the azimuthal compression in this flow leads to a free surface instability -- a crinkling or buckling in the azimuthal direction. This instability is suppressed by surface tension at large wavenumbers, and growth rates are strongly attenuated by solvent viscosity. A second analysis shows how thin stress boundary layers can develop in free surface flows, and the final analysis takes the stress localization idea literally, using as a model of a stress boundary layer a thin elastic membrane. Under elongation at constant enclosed volume, initially axisymmetric membranes with fixed circular ends, e.g., truncated cones, become unstable with respect to nonaxisymmetric disturbances, again due to azimuthal compressive stresses. The resulting configurations appear similar to those observed in filament stretching experiments.

Wednesday 5:30 Grand Terrace PO18

SIMULATION OF THE VISCOELASTIC FLOW OF MOLTEN PLASTICS

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Polymer melts exhibit some degree of viscoelasticity in industrial forming operations, and elasticity is particularly important in flows involving an abrupt contraction or expansion in the flow direction. However, the incorporation of a viscoelastic constitutive equation into computer models for polymer processing poses many problems, and for this reason inelastic models have been used almost exclusively to represent rheological behavior for flow simulation in the plastics industry. In this research, we tested two nonlinear viscoelastic models (Leonov and Phan-Thien/Tanner) in two types of complex flow and compared their predictions with those obtained using a strictly viscous model (Carreau-Yasuda) and with experimental results. Numerical instability was observed starting at quite low elasticity levels. Although satisfactory agreement with experimental results was obtained with both models for a converging flow, poor agreement was observed for a free surface flow. After exploring the limits of simulations using viscoelastic models, we conclude that there are serious barriers to progress in the simulation of viscoelastic flows of industrial importance. The ultimate source of the problem is the melt elasticity, and traditional numerical methods and rheological models do not provide a suitable basis for simulating practical flows. A new approach is required, and we propose that a rule-based expert system be used.

Wednesday 5:30 Grand Terrace PO19

ELASTICITY OF POLYMER NETWORKS

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Understanding the molecular mechanisms of rubber elasticity remains one of the most important unsolved problems of polymer physics. Numerous attempts to develop a molecular description of polymer networks in the last half of a century have been only partially successful and left the field with a dozen of competing and often conflicting models. Nevertheless several of these models introduce important physical concepts that describe many aspects of physics of polymer networks. We review what we believe are the most significant of these concepts and put them together into a coherent molecular picture of rubber elasticity.

Paper PO20 has been withdrawn. PO20

Wednesday 5:30 Grand Terrace PO21

INTERRELATION OF LIGAMENT CREEP AND RELAXATION

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Experimental data of Thornton, et al. show that relaxation proceeds more rapidly (a greater slope on a log log scale) than creep in ligament, a fact not explained by linear viscoelasticity. An interrelation between creep and relaxation is therefore developed for ligaments based on a single-integral nonlinear superposition model. This interrelation differs from the convolution relation obtained by Laplace transforms for linear materials. We demonstrate via continuum concepts of nonlinear viscoelasticity that such a difference in rate between creep and relaxation phenomenologically occurs when the nonlinearity is of a strain-stiffening type, i.e. the stress-strain curve is concave up as observed in ligament. We also show that it is inconsistent to assume a Fung-type (separable) constitutive law for both creep and relaxation. Using published data of Thornton, et al. the nonlinear interrelation developed herein predicts creep behavior from relaxation data well (R is 0.998 or better). Nonlinear viscoelasticity is known in polymers and in compact bone. In some cases, the nonlinear superposition approach appears adequate, but evidence has been found in some materials for time interactions describable by more general multiple integral constitutive relations.

Causal mechanisms associated with viscoelastic tissue behavior are complex. For example, in ligament, fiber recruitment gives rise to nonlinearity of a strain-stiffening type. Consequently, the stress-strain curve is concave up. The difference in creep and relaxation may also arise from different rates of tension driven fluid exudation and osmotically driven fluid imbibation. Regardless of mechanism, the present continuum analysis demonstrates that, based on continuum concepts, such nonlinearity causes relaxation to proceed more rapidly than creep. In a linear material, by contrast, power law creep and relaxation curves have the same slope.

Wednesday 5:30 Grand Terrace PO22

RHEOLOGICAL PROPERTIES OF PEANUT BUTTER

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The rheological properties of two different varieties of peanut butter have been studied, a suspension consisting of solid peanut particles in peanut oil, and a more complex type, consisting of the same suspension, stabilized and containing other ingredients in small quantities (sugar, salt). Peanut butter has been shown to be a concentrated suspension of solid particles in a Newtonian medium (peanut oil, η=70 mPa.s at 24°C). The solid particle diameter has been determined via both optical and electronic microscopy. A mean average diameter of 6.6 μm was obtained, with a relatively narrow size distribution (polydispersity of 1.7). The volume fraction has been estimated to be about 0.6. In this experimental study, very serious problems due to slip at the walls have been encountered, leading to important differences in the rheological measurements with changes in gap size. These problems have been solved using sand paper glued to the parallel plates of the rheometer. From plots of the flow curve in stress growth and from creep experiments yield stress values of about 30 and 250-300 Pa have been obtained for the non-stabilized and stabilized suspension, respectively. Both suspensions were found to be highly shear-thinning. For the stabilized suspension, the elastic modulus is larger than the loss modulus, suggesting strong particle-particle interactions. The stabilizer plays a major role on the viscoelastic and transient properties of peanut butter. Moreover, the viscoelastic response for the stabilized suspension is non-linear for strain amplitude above 0.01. Possible mechanisms responsible for the behavior of peanut butter will be discussed.

Wednesday 5:30 Grand Terrace PO23

VISCOELASTICITY OF GELATIN BLENDS FROM ALTERNATIVE SOURCES

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Gelatin is a very important biopolymer which has found widespread use in the food and photographic industries over the years. Since most of the available commercial gelatins are derived from bovine and porcine sources, there has been considerable interest in using alternative substitutes. This has especially been the case since the recent UK BSE (bovine spongiform encephalopathy) crisis.

As described in Abstract SG1, the melting and gelling temperature of gelatin has been found to correlate with the imino acid residues in the original collagen[1]. Cold water fish , for example cod collagen, has a very low hydroxyproline content and coupled with this is a very low gelling and melting temperature. 10% mammalian gelatin forms a gel at ~room temperature, whereas 10% cod will only gel at ~2°C. In this poster, we examine blends of both (a) mammalian and fish and (b) different fish species gelatins and investigate how the properties of the single systems are altered in the blends.

Measurements have been used to characterise the gelling and melting temperatures and G'. Fish samples studied were tilapia, tuna, megrim and cod, ranging in order from tropical to cold water. Results indicate so far that in mammalian/fish mixtures, no significant difference in properties from the single systems is seen with the warm water fish blends i.e. tuna and tilapia. With the cold water fish blends however, notably cod, the modulus and melting points of the mixtures are raised considerably even in the presence of a small concentration of mammalian gelatin. Since the cod however is non-gelling under standard conditions (8°C), future work will investigate whether the blend is merely a mammalian gel swollen by a cod sol.

REFERENCES 1. Veis, A., The Macromolecular Chemistry of Gelatin, Academic Press (1964).

Wednesday 5:30 Grand Terrace PO24

RHEOLOGY OF PARAFFINIC OILS

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High paraffin content crude oils, when cooled, undergo a dramatic increase of their viscosity or even the formation of a gel which may lead to the plugging of lines and restarting problems. An efficient processing of such heavy crude oils requires a thorough understanding of their rheology. In this work we investigate the rheology of heavy paraffinic oils in both flowing and quiescent conditions. A waxy crude oil with about 20 wt% of C10+ paraffins was supplied by Elf EP. The amount of crystallised material was determined, as a function of temperature, by Differential Scanning Calorimetry (DSC). For rheology measurements we used a stress-controlled rheometer (TAinstruments AR1000) with a cone-and-plate roughened geometry to avoid wall slip. Oscillatory experiments showed a transition from a liquid to a strong gel in a narrow temperature range. In the flowing regime we studied the effects of parameters such as shear rate and shear stress. Imposing a steady shear rate or shear stress during cooling led to markedly different behaviours. To account for the equilibrium viscosity at a given temperature and shear rate we combine suspension and aggregation under shear models. Finally, fracture of the gel was studied by creep and oscillatory tests. In both methods the fracture occurs after creep or plastic deformation with the extent of strain being the critical parameter.

Wednesday 5:30 Grand Terrace PO25

SHEAR-INDUCED OSCILLATIONS OF DYNAMIC MODULUS IN POLYMER GELS

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In polymer solutions, an application of a shear field can induce migration of a polymer. In the cone-and-plate geometry, concentration of the polymer decreases near the edges; i.e. a polymer migrates towards the central region. After stopping the shear, this spatial inhomogeneity should recover via diffusion of the polymer. In viscoelastic polymer systems, the process of recovery can be manifested as an evolution of an elastic modulus G'. We observed oscillations of elastic modulus G' after shear for gels prepared from polyacrylate solution with dispersed silica particles. After preshear (3 min at 500 $\sec^{-1}$) with a stress-controlled rheometer, the dynamic time sweep was performed at frequency 1 Hz and very small stress amplitude. We monitored a time evolution of G'(t) for 1-2 h. The value of G'(t) changed periodically with the period increasing with time. The amplitude of oscillations did not change with the recovery time, however, it depended strongly on the pH of gels. In the pH range of 4.3- 7, the amplitude increased by a factor of 5. In the controlled stress mode, a small constant static stress was applied to the gels while measuring G' using small amplitude dynamic stress. In this case, the period of oscillations decreased with increasing static stress. This effect is typical for classical oscillators like strings in musical instruments. By means of this analogy, periodic oscillations of the shear stress in the gel confined between the cone and plate could explain our observations.

Wednesday 5:30 Grand Terrace PO26

VISCOELASTICITY AND SHEAR THINNING IN XENON

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Microscopic density fluctuations become extraordinarily slow near the liquid-vapor critical point. This allows the observation of viscoelasticity and shear thinning in a fluid as simple as xenon. We recently used a novel, overdamped oscillator to measure the viscosity of xenon near its critical density and temperature T_c. The measurements spanned frequencies f from 2 Hz to 12 Hz and they revealed viscoelasticity within 3 mK of T_c, where the imaginary component was as large as 3% of the real component. The frequency dependence scaled as a function of Aft, where τ is the characteristic decay time for a critical fluctuation, and the fitted value of A was 2.0 ± 0.3 times the predicted result. The measurements were conducted in microgravity aboard the Space Shuttle because normal gravity causes the xenon's density to vary with height in the sample.

We are preparing a similar microgravity experiment to measure shear thinning in xenon. Shear thinning has never been observed in a pure fluid composed of small molecules because, except very near the critical point, the internal relaxation times are too short. By increasing the viscometer's amplitude by a factor of 30, the experiment will produce data with scaled shear rates St as large as 100, where S is the shear rate. As much as 5% shear thinning is expected in the limit of low frequency. Many of the data will be taken with both St >>1 and ft >>1, for which there is no theory. An opportunity exists to extend well-established rheological models to a near-critical pure fluid.

Wednesday 5:30 Grand Terrace PO27

DETERMINATION OF NONLINEAR VISCOELASTIC PROPERTIES OF WHEAT DOUGH BY LARGE AMPLITUDE OSCILLATORY SHEAR (LAOS) TEST

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During many food preparations, wheat dough undergoes complex and nonlinear rheological processes. Many researchers have reported wheat dough properties related to linear viscoelasticity using a small amplitude oscillatory shear (SAOS) test. For nonlinear viscoelasticity, Instron-type uniaxial or biaxial rheometer is traditionally used. But such instruments cannot operate at conditions similar to those during mixing, kneading, baking, and extruding. The sliding plate rheometer (SPR) can generate a homogeneous shear flow for nonlinear viscoelastic condition and outperform traditional rheometers in polymer processing. It also minimizes slip and moisture loss problems during testing. The objectives of this research were to evaluate the nonlinear viscoelastic parameters of wheat flour dough using the SPR and to compare the results with those obtained from SAOS tests.

Wheat flour dough was prepared (46% moisture content) and subjected to strains ranging from 0.2 to 10 at frequencies ranging from 0.1 to 10 Hz. The shear strain conditions were set based on the gap of 0.36 mm (= the height of sample after loading). The stress responses were analyzed by discrete Fourier transformation and converted into ellipsoidal strain-stress loops. The relaxation spectra from SAOS were used as a component of the Wagner constitutive model. The nonlinear viscoelasticity was determined at strain levels higher than 0.00143. Damping function was determined to characterize the nonlinear viscoelasticity of wheat flour dough at strain levels up to 10. The relaxation moduli were estimated but in a limited range.

Wednesday 5:30 Grand Terrace PO28

EVALUATION OF STRUCTURE DEVELOPMENT DURING GELATION OF XANTHAN AND CAROB MIXTURES

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Gelation mechanisms of thermoreversible gel mixtures are complex and difficult to describe quantitatively. This is mainly due to different processes involved such as association of different polymers and aggregation of polymer strands. In addition, these processes are strongly dependent on the temperature as well as ratio of mixture components. The objectives of our study were to: 1) describe the synergistic effect between xanthan and carob in the mixed gel system, 2) determine gelation temperatures as a function of total polymer concentration and mixture ratio, 3) quantify effect of temperature on gelation of thermoreversible gels, and 4) analyze the gelation mechanism based on thermorheological behavior.

Laboratory grade xanthan (X) and carob (C) were used at three total polymer concentrations (0.1, 0.5, 1.0 g/100 mL) and five X/C mixture ratios (0:1, 1:3, 1:1, 3:1, 1:0). Small amplitude oscillation tests were performed (0.01 to 10 Hz) to measure linear viscoelastic behavior during gelation using a Bohlin CVO dynamic rheometer. Temperature sweep (1°C/min; 0.1 Hz) was performed to monitor thermorheological behavior of the gel system.

Gelation temperature (Tgel) was determined to be about 55°C. The Tgel was independent of X/C ratio but increased slightly with increase in total polymer concentration. The synergistic effects, as measured by the increase in storage and loss moduli, were a strong function of X/C ratio. The apparent activation energy of 1:3-, 1:1-, and 3:1-X/C mixtures was 178.8, 159.2, and 123.2 kJ/mol, respectively. Based on the discontinuity in the activation energy plots, two gelation mechanisms were believed to occur - the association of xanthan and carob molecules and aggregation of polymer strands. The association and aggregation processes were rate-determining step for the initial (55-43°C) and final (33-25°C) stages of gelation, respectively.

Wednesday 5:30 Grand Terrace PO29

RHEOLOGICAL CHARACTERIZATION OF MILK GELATION USING VEGETABLE COAGULANTS AND CHYMOSIN

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Milk gelation results from the aggregation of casein micelles which are destabilized by the action of an enzyme, such as chymosin. After the onset of coagulation there is a progressive increase in gel firmness. When the coagulum reaches a certain stiffness, which is usually determined empirically by the cheese maker, it is cut to expel the whey. Cutting the coagulum at an optimal firmness is crucial to minimize loss of milk fat and curd fines in the whey, and to maximize cheese yield. Therefore, it is critical that the coagulation process is controlled properly. One of the recent trends in cheese making is to use coagulants other than chymosin either to impart specific characteristics to the cheese or for economic reasons. In this study, we compared the milk coagulation process using vegetable coagulants (Cynara humilis L. and Cynara cardunculus L.) and chymosin using small amplitude oscillatory shear tests. The results show that even after the time usually considered adequate for cutting, G' values of the milk gels obtained using the vegetable coagulants were higher than those for the milk gels coagulated with chymosin. In cheese making a good coagulant is that which makes a firm gel. On this basis, the vegetable coagulants we tested seem to exhibit coagulation characteristics similar to those of the chymosin. Mathematical models were developed to describe the experimental G' values of milk coagulation as a function of time and the suitability of two published models, those of Scott Blair and Douillard, were tested. The relative activities of the enzymes were compared in terms of the model parameters.

Wednesday 5:30 Grand Terrace PO30

THERMOREVERSIBLE GELATION OF METHYL CELLULOSE A4M SOLUTIONS

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The thermoreversible gelation behavior of aqueous methyl cellulose solutions was determined using temperature ramp experiments. A4M, a commercial grade of methyl cellulose, was studied over a range of concentration from 0.21 to 2.34%. A Rheometrics ARES fluids spectrometer equipped with a Couette sample geometry and a 100 g-cm FRT torque transducer was used was used in both the steady shear and low strain, oscillatory mode. Temperature ramps were performed at a rate of 1° Celsius per minute starting from 20ºC, going to 65ºC, and then returning to the starting temperature. A frequency of 1 rad/second at low strains was used to monitor changes in the fluids throughout the experiment.

The samples ranged in viscosity at 25ºC from 10 cP to 7,530 cP with good agreement between the steady shear and the dynamic viscosities. Upon heating, the viscosity of each sample initially dropped at the same relative rate. Above 55ºC, this changed to a rapid increase in dynamic viscosity referred to as the "take off" or gelation temperature. All the take off temperatures happened between 55 and 60ºC and were inversely related to concentration. On cooling the samples "melted" over a 5-degree temperature range centered about 33ºC.

From a plot of zero-shear viscosity at 25ºC versus polymer concentration the viscosity-concentration scaling exponents were obtained. They indicate the sample set covers the range from dilute to concentrated solution. The gelation and melting temperatures were found to correlate well with the viscosity at 25ºC. These results will be discussed and contrasted with results from experiments on gelatin in water solutions.

Wednesday 5:30 Grand Terrace PO31

SALT EFFECT ON DNA OLIGOMER BINDING IN SELFASSEMBLED NANOSTRUCTURES

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Unique recognition ability of DNA to bind to complement oligomer is utilized in various technological applications of "smart" or "intelligent" materials. Relatively short, 10-100 base pairs, DNA oligomers attached to solid nanoparticles cause particles assembly in spatial structures and alteration of physical and rheological properties of materials. This assembly process is reversible and controllable by change in salt concentration of surrounding (carrying) fluid. The "effectiveness" of the process (fraction of bound oligomers) is directly connected to electric field and counterion distribution around DNA oligomer. In this presentation, an electric field in cylindrical symmetry around an oligomer of finite length is determined numerically and analytically from the Poisson-Boltzmann equation for electrolytes. Numerical results are obtained for single- and double-stranded DNA oligomers (radiuses 7 and 10 Å correspondingly) of lengths 25-150 Å in salt concentration range 0.01-0.2 M. Approximate analytical solution is obtained by boundary layer approach under following conditions: length of oligomer is bigger than its diameter and salt concentration is high enough (bigger than 0.01 M for double-stranded DNA). Both numerical and analytical solutions are in good agreement. These results allow prediction of change in fraction of bound DNA oligomers with change in salt concentration for given physical conditions, concentrations of reacting oligomers, and their lengths and charges.

Wednesday 5:30 Grand Terrace PO32

EVIDENCE OF CHAOTIC REGIMES IN NUMERICAL SIMULATIONS OF THE DOI THEORY FOR LIQUID CRYSTALLINE POLYMERS

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The three-dimensional Doi equation for the time dependent orientational distribution function of rod-like macromolecules is solved in simple shearing flow conditions. The rotational diffusivity is assumed to be constant. Such simplification permits the use of the Galerkin procedure for the numerical integration, where the distribution function is developed as a truncated spherical harmonics series. The results are compared with those obtained with a simplified constitutive equation where a closure approximation is introduced. Emphasis is given on the presence of apparent chaotic regimes detected both in the Doi model and the approximated constitutive equation in the same range of parameter values and initial conditions.

Wednesday 5:30 Grand Terrace PO33

MODELING EVOLUTION OF MICROSTRUCTURE IN DISCOTIC MESOPHASE PITCHES UNDER SHEAR

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Mesophase pitches are discotic liquid crystals and forms an important class of low cost precursor materials that are used to manufacture high performance mesophase pitch-based carbon fibers. These industrial fibers possess exceptional mechanical and thermal transport properties; they exhibit ultra high Young's modulus, low density, extremely large thermal conductivity, and negative coefficient of expansion, and are increasingly being employed in the next generation composite materials for the aerospace, the electronics and the automotive industries. The superior properties of mesophase carbon fibers depend on the microstructure that evolves during the spinning process, and which is a function of the operating conditions, geometry, and material properties. There has been a great interest in understanding the texture evolution during the fiber formation melt spinning process in which the mesophase pitches are subjected to non-homogeneous mixed shear and extensional flows. In this work flow modeling of model mesophase pitches is performed using a complete phenomenological theory that takes into account short range and long range order elasticity, and viscous flow effects. The present theory is fully compatible with the well-known Leslie-Ericksen and Doi theories, and thus fills the parametric gap where these classical theories are inapplicable. The microstructural response of "model" mesophase pitches under rectilinear shear flows

is simulated, and the numerical results are used to identify and characterize the novel relations among rheology, microstructure and processing conditions.

Wednesday 5:30 Grand Terrace PO34

A CONSTITUTIVE MODEL FOR THE BEHAVIOR OF SEMI-FLEXIBLE RODS IN SHEAR FLOW

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A straight slender body executing its Jeffery orbit in Newtonian Couette flow at vanishingly small Reynolds number is subject to purely axial fluid forces, alternating between compression and tension. For sufficiently strong flows, the rod will buckle. We present a stability analysis of this problem, which indicates that buckling may occur in practice for macroscopic continuum fibers suspended in a viscous solvent at high shear; for less-rigid semi-flexible biopolymers such as actin this viscously-driven growth of bending modes is especially relevant under common experimental conditions. Buckling also leads to net normal stresses over one orbit as well as a translation across streamlines, but does not appear to modify the rotation rate for small-amplitude disturbances. We also derive Smoluchowski-type equations for the rotation and bending modes subject to random forcing including non-local hydrodynamic interactions, and investigate numerically the evolution of the probability distributions and the corresponding rheological properties.

Wednesday 5:30 Grand Terrace PO35

FIRST OBSERVATION OF THE ISOTROPIC-NEMATIC PHASE TRANSITION TEMPERATURE OF LIQUID CRYSTALLINE POLYMERS ON TWO-DIMENSIONAL LANGMUIR MONOLAYERS

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The isotropic-nematic transition of liquid crystalline polymers in three dimensions has been studied extensively. The transition, known as the first order in three dimensions, occurs at a specific temperature that is called the isotropic-nematic phase transition temperature, TIN. However, no study about TIN in two dimensions has been reported. The purpose of this paper is to examine molecular orientational hydrodynamics through studies of monolayer films at the air-water interface and to understand the phenomena of phase transition in two dimensions. UV absorption spectroscopy is used to determine molecular orientation on hairy-rod 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 solvent of stearic acid (SA) at moderate concentrations is added to this polymer solution to fluidize the film. At high temperature, complete relaxation of molecules is observed after flow cessation. At a lower temperature, a nematic ordered phase is obtained. The isotropic-nematic phase transition temperature, TIN is about 29oC at 40mol% PPPSH/SA mixture. Measurements of the surface modulus and surface viscosity were also performed to investigate the phase transition. The result of order parameter over temperature proposes that the isotropic-nematic phase transition in two dimensions is the second order.

Paper PO36 has been withdrawn. PO36

Paper PO37 has been withdrawn. PO37

Wednesday 5:30 Grand Terrace PO38

MEASURING THE ZERO-SHEAR-RATE VISCOSITY USING SQUEEZE FLOW AND INTERFERENCE FRINGES

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The development of single-site catalysts has made a significant improvement in controlling the molecular structure, and thus, the rheology of "metallocene" polyethylenes. However, the measurement of linear viscoelastic properties at low frequencies has been historically problematic for polyethylenes owing to their time-temperature shift factors that are close to unity. Access to these long time scales is important because they dictate the elastic behavior of the melt and provide information about the high-MW tail of the MWD. Solving for the "viscosity MWD" suffers from poor data in the low-frequency region resulting in secondary peaks in the high-MW tail of the MWD. A simple but effective squeeze flow apparatus employing interference fringes that measures zero-shear-rate viscosity was presented [Cua, E.M.C., Shaw, M.T., New Approach in Measuring Low-Frequency Viscoelastic Properties, SOR 70th Annual Meeting]. An optical flat and a plano-convex lens serves as the bottom and top "plates" respectively, with the latter being unconstrained laterally. Improvements in the design along with results for PDMS (SE-30) at room temperature are now available. It was found that slight deviations in tilt of the normal vector of the bottom plate with respect to the gravity vector resulted in appreciable lateral movement of the upper plate and increased the gap velocity, seriously decreasing the measured viscosity.

Wednesday 5:30 Grand Terrace PO39

STRUCTURAL AND VISCOELASTIC PROPERTIES OF LAMELLAR SYSTEMS FORMED FROM CONCENTRATED NONIONIC SURFACTANT SOLUTIONS

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The structure and rheological properties of concentrated lamellar system of wthoxylated alcohol - water binary mixtures were investigated. The structure of samples was investigated by polarization light microscopy, SAXS measurements and by transmission electron microscopy. Investigating the rheological properties, it was found that in the linear viscoelastic region the shape of the storage and loss modulus vs. frequency curves are specific and characteristic to the lamellar systems. The storage modulus increases slightly and the loss modulus goes through a minimum with increasing frequency. The sample is mainly elastic thoughout the whole investigated frequency range. The surfactant type, concentration and temperature have strong influence on the frequency dependent viscoelstic properties. The structure becomes more elastic with lowering the temperature and tan delta goes through a minimum with increasing surfactant concentration. Investigating the effect of surfactant type on the rheological properties it was found that the tan delta depends both on the hydrophobic chain length and on the ethoxylation number. Both the storage and loss moduli were found to be sensible to structural changes of the sample, such as the ordering of lamellae with increasing concentration, or the melting of the carbon chains of the surfactants with increasing temperature. The storage and loss moduli versus frequency can be well described by fitting the slip-plane theory of Jones and McLeish if it is modified by an additional term which is needed probably due to the presence of non slip plane like distortions present in the sample. This means that strong ordering of lamellae should occur due to the shear even in the linear viscoelastic region. The ordering tendency of lamellae was also deduced by observing the pseudo isotropic behaviour of the samples i.e. that they order parallel to he plane of the microscope slide.

Wednesday 5:30 Grand Terrace PO40

TIME-RESOLVED TRANSIENT VISCOUS FLOWS OF A NEWTONIAN DROP IN A NEWTONIAN LIQUID

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The time resolved evolution of a liquid drop immersed in an liquid matrix is studied under transient flow conditions. The two phases consist of two immiscible fluids. The drop is Newtonian and buoyancy free; the external liquid is Newtonian, and subjected to a flow history. Three different flow conditions are considered: Step-up, step-down, and flow-reversal experiments. Three different viscosity ratios are investigated so that a rather complete picture of the involved phenomena is obtained. The experimental results are interpreted with a phenomenological theory. The agreement between experimental results and the predictions is good. The results can also be used to explain some stress features typical of immiscible polymer blends available in the literature.

Wednesday 5:30 Grand Terrace PO41

A PRESSURE PROFILE SYSTEM FOR MEASURING THE FIRST AND SECOND NORMAL STRESS COEFFICIENT OF NON-NEWTONIAN FLUIDS

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Due to the lack of readily available and sufficiently sensitive pressure measuring devices, the second normal stress coefficient has not been widely reported in the past. In the present work, the radial pressure profile across the base of a cone and plate rheometer is investigated using a highly sensitive 16-element flush mounted sensor array of 2mm x5mm capacitive transducers. The radial pressure distribution across a cone and plate rheometer resulting from a constant applied shear stress is a function of both the first and second normal stress coefficient of the tested fluid and can be represented in the form $P(r) = F_1(\Psi_1,\Psi_2,\ln[r/R]) + F_2(\Psi_2)$. Extrapolation of the pressure to the value at the outer edge of the cone is used to calculate the second normal stress coefficient, and determination of the slope can be used to subsequently deduce the first normal stress coefficient. The device is also a very sensitive probe of axial misalignment between the cone and plate which leads to pronounced deviations from a radially symmetric pressure distribution. To demonstrate the flexibility of the present sensor design we use this pressure profile system to determine the second normal stress coefficient in a dilute Polystyrene boger fluid, a semi-dilute entangled solution of the same monodisperse polystyrene solute, and a concentrated suspension of monodisperse hard spheres. In addition we show that the system can be used to monitor the transient and non-monotonic evolution of the pressure profiles at the base of granular heaps and silos.

Wednesday 5:30 Grand Terrace PO42

MEASUREMENT OF NORMAL FORCES AT THE INTERFACE OF TWO IMMISCIBLE LIQUIDS USING DIGITAL IMAGE ANALYSIS

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An apparatus is designed to measure normal forces at the interface of two immiscible liquids in a Couette flow. The system is composed of a liquid bridge containing a polystyrene solution rotating in a cylindrical bath filled with an immiscible Newtonian liquid of almost identical density. The curvature of the interface is determined using digital image analysis (PSI-A) to derive the difference of the pressure across the liquid-liquid interface.

The experiments show the expected parabolic dependence of the normal force at the interface over the length of the liquid bridge. A quadratic relationship of the measured normal force with the rotation rate is found which fits theoretical considerations. The results are compared with a system where both liquid bridge and bath liquid are

Newtonian to exclude centrifugal effects. The effect of small density variations of the two liquids is considered. The results are further compared with an simplified analytical model of the system.

Wednesday 5:30 Grand Terrace PO43

INSTABILITY OF THE DOI-EDWARDS MODEL IN SIMPLE FLOWS

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A stability characteristic of the Doi-Edwards viscoelastic constitutive equation is studied. Hadamard-type stability determined by the part of quick response in the constitutive equation is considered in the case of simple flows. Criteria for general 3-D stability are derived in a complete biquadratic form, and rather simple algebraic condition under 1-D and 2-D disturbances is then formulated. Application of constraints to this rheological equation of state proves inevitable occurrence of the Hadamard-type instability in simple shear and uniaxial (or equi-biaxial) extensional flows, and the threshold of instability is calculated in terms of instantaneous strain for all the flow types. The obtained values of critical strains are relatively low, hence it is thought that they can be easily achieved even in moderate experiments as well as in industrial processing. We conclude that this instability seems not related to real physical phenomena at all and it is merely inappropriateness inherited by the constitutive equation.

Wednesday 5:30 Grand Terrace PO44

SHEAR INDUCED POLYMERIZATION: A DIRECT DEMONSTRATION

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The control of the molecular weight of macromolecules is of paramount importance in pharmaceutical applications, biotechnology, and polymer processing. Here, we use DNA molecules with cohesive ends (sticky ends) as a model system to study the new physics of shear-induced polymerization. Using analytical gel electrophoresis and fluorescence microscopy, we show that DNA molecules form integral multimers of increasing molecular weight for increasing shear rates. We verify that the shear flow, which favors inter-chain interactions via connection of the cohesive ends of the polymers, induces the assembly. These unexpected results reveal a new and fundamental insight into the behavior of associating polymers under shear and may form the basis of a novel approach to control polymer assembly in recombinant DNA technology and polymer science.

Wednesday 5:30 Grand Terrace PO45

THERMO-MECHANICAL DEGRADATION IN THE PREPARATION OF POLYETHYLENE BLENDS

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A Rheocord 90 melt blender was used to prepare samples intended for study of the melt rheology and miscibility of blends of HDPE, different LLDPEs and LDPE as well as to condition the pure components. The objective of this study was to make sure that the thermo-mechanical degradation of polyethylenes was prevented during the "conditioning" process.

Different techniques were employed to examine the stability of melts conditioned in the blender. Samples were characterized by dynamic viscosity as well as by average molecular weight and MWD from GPC analysis, both before and after the blender experience. The rheological and GPC analyses were complemented by NMR, DSC, and TREF testing. The study included "conditioned" resins with and without additional antioxidants; results were compared to the properties of as-received polymers. The different techniques integrate to explain: the modifications that can occur due to melt blending of polyethylenes; relationships to the polymer chemistry (saturation, branch content); and possible means for detection and prevention of degradation. Addition of adequate amounts of antioxidant is successful in prevention of degradation.

HDPE and LDPE samples, used in this study, were found to be stable even without extra antioxidant. Ziegler-Natta and metallocene LLDPE mixed at 190 and 220C showed different levels of degradation depending on blender

conditions (temperature, presence of antioxidants, nitrogen blanket) and polymerization catalyst. Enhancement of the dynamic viscosity of "conditioned" resins over that of the as-received resins correlated with branch content and branch length of the LLDPE, with metallocene LLDPE showing higher susceptibility to degradation.

Wednesday 5:30 Grand Terrace PO46

USING FILAMENT STRETCHING RHEOMETRY TO PREDICT STRAND FORMATION AND "PROCESSABILITY" OF ADHESIVES AND OTHER NON-NEWTONIAN FLUIDS

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The spinning of polymeric fibers, the processing of numerous foodstuffs and the peel & tack characteristics of adhesives is associated with the formation, stability and, ultimately, the longevity of thin fluid 'strands'. This tendency to form strands is usually described in terms of the tackiness of the fluid or by heuristic concepts such as 'stringiness' [Lakrout et al., J. Adhesion 69, 307 (1999)]. The dynamics of such processes are complicated due to spatially and temporally non-homogeneous growth of extensional stresses, the action of capillary forces and the evaporation of volatile solvents. In this poster presentation we describe the development and application of a simple instrument referred to as a microfilament rheometer (MFR) that can be used to readily differentiate between the dynamical response of different pressure-sensitive adhesive fluid formulations. The device relies on a quantitative observation of the rate of extensional thinning or 'necking' of a thin viscoelastic fluid filament in which the solvent is free to evaporate across the free surface. This high-resolution measurement of the radial profile provides a direct indication of the ultimate time to break-up of the fluid filament. This critical time is a sensitive function of the rheological properties of the fluid and the mass transfer characteristics of the solvent, and can be conveniently reported in terms of a new dimensionless quantity we refer to as an Adhesive number. We demonstrate the usefulness of this technique by presenting our results in the form of a case study in which we measure the visco-elasto-capillary thinning of slender liquid filaments for a number of different polymer/solvent formulations and relate this to the reported processing performance of the materials. We also compare the MFR observations with the prediction of a simple 1D theory derived from the governing equations that model the capillary thinning of an adhesive filament.

Wednesday 5:30 Grand Terrace PO47

A PRELIMINARY INVESTIGATION OF AN ELECTRORHEOLOGICAL LUBRICANT

Brent M. Roberts and Frank E. Filisko
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The experimental results of the feasibility of using electrorheological (ER) fluids as lubricants are presented. Lubricants involving ER fluids are termed "smart" lubricants, which are materials whose viscosity can be reversibly, rapidly and dramatically changed by the application of electric fields. The criterion for this phenomenon is based on the accepted Stribeck curve, which describes the frictional losses between sliding surfaces. In this case, the "smart" lubricant consisted of poly(sodium-4-styrenesulfonate) particles suspended in paraffin oil at a concentration of 20 wt%. With the addition of an electric field of 800 V, the "smart" lubricant showed a decrease in fiction at low shear rates compared to the same fluid under no electric field.

Wednesday 5:30 Grand Terrace PO48

THE EFFECT OF SMALL AMOUNTS OF ADDED SECONDARY PARTICLES TO AN ELECTRORHEOLOGICALLY ACTIVE SUSPENSION

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The shear stresses of a base ER suspension, poly(sodium-4-styrenesulfonate) in mineral oil, and the base ER suspensions with small amounts (1 weight percent) of added secondary particles were evaluated using a couette apparatus rotated at 180 rpm under various E fields. The biparticulate systems displayed an increase in shear stress over the base system at high E fields. The flow profiles of the biparticulate systems revealed a segregation of the secondary particles and the base ER particles with the secondary particles occupying the area between ER active lamellar structures.

Wednesday 5:30 Grand Terrace PO49

CHARACTERIZATION OF COMMERCIAL POLYETHYLENE MELTS USING TRANSIENT EXTENSIONAL VISCOSITY AND STEADY SHEAR FLOW CURVES

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Three families of commercial polyethylene resins and one commercial linear polypropylene resin were rheologically characterized in transient elongation and steady shear flow. The polyethylene resin families were categorized according to the catalyst system used to synthesize them: Ziegler-Natta, Phillips process chromium catalyzed and free radical polymerization. The Ziegler-Natta catalyst systems yield polydisperse linear polymers. The Phillips process chromium catalyzed resins are comprised of predominantly polydisperse linear, and small amounts of 3-arm star and multi-toothed comb polymers. The small weight fraction of comb polymer present provides the enhanced elasticity and extension hardening observed in transient extension. To model these resins, we considered the Phillips resin to be analogous to a Boger fluid, where small weight fractions of very high molecular weight linear polymer generate all the elasticity. Thus, we sought to mimic the rheological behavior of the Phillips resin with a system of mostly linear polydisperse polymer with a small weight fraction of very high molecular weight polymer. The elastic contribution to the melt is provided by the spike of ultra-high molecular weight polymer rather than the comb. The recently developed binary interaction model is a viable constitutive model for polydisperse linear polymers(1). The theory can be legitimately applied to systems of linear polydisperse polymer. The theory was then tested with real and simulated Phillips resins. The optimal composition of the model Boger type fluid used to best fit the data can be used as a "figure of merit" to quantify the degree of long chain branching present in a resin.

Wednesday 5:30 Grand Terrace PO50

SMALL-ANGLE X-RAY SCATTERING OF SHEAR FLOW ORIENTED SELF-ORGANIZED HIERARCHICAL POLYMERIC NANOSTRUCTURES

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We have recently demostrated self-organized supramolecular polymeric nanostructured materials that show order at multiple length scales (1). In this work we present our efforts to macroscopically orient such hierarchical structures by oscillatory shear flow as characterized by using in-situ small angle X-ray scattering (SAXS).

References: 1. J. Ruokolainen, R. Mäkinen, M. Torkkeli, R. Serimaa, T. Mäkelä, G. ten Brinke and O. Ikkala, Science 280, 557, 1998

Wednesday 5:30 Grand Terrace PO51

DEVELOPMENT AND USE OF A NOVEL CONE AND PLATE FLOW CELL FOR X-RAY SCATTERING STUDIES OF MATERIALS FROM THE VORTICITY PLANE: PRELIMINARY RESULTS FROM A 13.5WT% PBG/M-CRESOL SOLUTION

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The evolution of structure in liquid crystalline polymers during shear has a critical effect on their rheological behavior. In this work we present a novel annular cone-and-plate flow cell which permits in situ x-ray scattering from the 1-2 plane during shear flow. The development of structure in LCPs has been extensively studied using a variety of in situ scattering techniques to provide certain projections of structure of the material. Previous in situ x-

ray scattering studies have focused primarily on the 1-3 plane of the flow. The 1-2 projection potentially holds more information about the fluid structure than the 1-3 plane. Preliminary results of experiments with 13.5 wt% racemic poly(benzyl glutamate) in m-cresol during steady shear flow, transient shear protocols, and oscillatory flow will be presented.

Wednesday 5:30 Grand Terrace PO52

MORPHOLOGICAL TRANSITION IN SHEARED POLYMER BLENDS: THE INTERPLAY OF COALESCENCE, BREAKUP AND FINITE SIZE

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We report the observation of a shear induced morphological transition in concentrated polymer blends which occurs when the system thickness becomes comparable to the droplet size of the dispersed component. Above a critical shear rate, we observe coalescence and breakup; a living equilibrium in which large droplets break up into smaller ones, and smaller droplets coalesce into larger ones. As the shear rate is reduced below a critical value, droplets coalesce and form into stable strings, with aspect ratios as large as 10^4. The transition is sharp, occurring over a shear interval of as little as 5 %. Increasing the gap size yields a decrease in the critical shear rate, as well as an increase in the critical droplet size. The transition is generic as we have observed it in viscosity ratios ranging from 0.1 to 10, as well as over a range of elasticity ratios. The transition is a manifestation of the weakening of the Rayleigh-Tomatika instability as the system becomes quasi two-dimensional.

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