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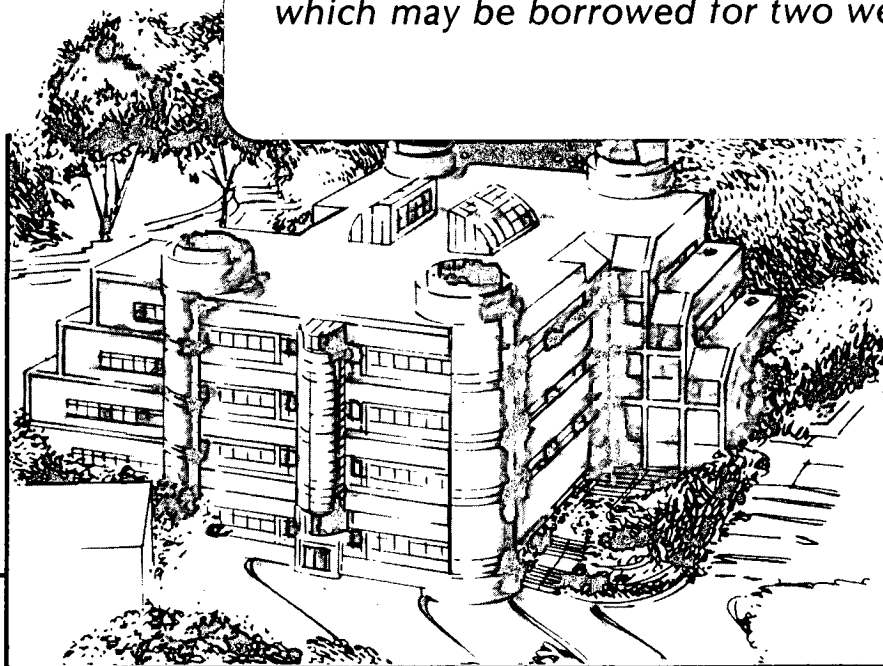Processing and Manufacturing, Boston, MA,
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Fluid Mechanical Issues in Polymer Processing

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FLUID MECHANICAL ISSUES IN POLYMER PROCESSING

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ABSTRACT

Microstructure in polymers is developed during shaping operations which
are carried out in the fluid state. Propagation of the large stresses caused
by singularities associated with the flow of viscoelastic liquids near corners
and lips is a limiting factor in the numerical solution of processing flows;
the strength of the singularity is unknown. There is considerable evidence to
indicate that the no-slip boundary condition is inappropriate in polymer
processing flows, but the proper replacement has not been established. Other
significant issues include flow instabilities and the analysis of the flow of
anisotropic liquids.

INTRODUCTION

Polymeric materials are used in the solid phase, but many of the end-use
properties are determined by microstructure that is developed during fluid-
state shaping operations. These shaping operations (injection and compression
molding, fiber spinning, extrusion, etc.) generally involve flow through
complex geometrical shapes, and often include free-surface flows; the flow is
accompanied by very large temperature changes, usually at extremely high rates
of cooling. Solidification occurs as part of the processing operation, and the
solid phase morphology is dependent on the processing history of the liquid.

The distinguishing characteristic of polymeric liquids is that they are
viscoelastic; that is, the stress state depends on the entire history of
deformation of a material element. Stress constitutive equations for solutions
and melts of flexible polymers have been derived from both phenomenological and
quasi-molecular considerations (e.g., 1, 2, 3). The most elementary repres-
entation of the stress in a polymeric liquid is contained in the *Maxwell
liquid*,

$$\lambda \left[\frac{\partial \tau}{\partial t} + v \cdot \nabla \tau - \tau \cdot \nabla v - (\nabla v)^\dagger \cdot \tau \right] + \tau = \lambda G \, [\nabla v + (\nabla v)^\dagger] \tag{1}$$

Here τ is the extra-stress, v is the velocity, and λ and G are material con-
stants, known as the relaxation time and the shear modulus, respectively. The
shear viscosity, η, is equal to the product λG. The extra-stress is not devia-

toric (i.e., trace $\tau \neq 0$; indeed, trace τ is proportional to the entropic free energy associated with the deformation). This fluid model shows exponential relaxation of stresses after shearing, normal stresses during steady shearing that vary with the square of the shear rate, and a constant viscosity.

Real polymeric liquids typically show quadratic normal stresses and a constant shear viscosity only at very low deformation rates. The viscosity of the Maxwell liquid in steady extension is a monotonically increasing function of extension rate, and becomes unbounded at a finite stretch rate equal to $1/2\lambda$; real polymeric liquids show bounded extensional viscosities, and the extensional viscosities of polymer melts rarely exceed the zero-shear viscosity by more than an order of magnitude, though differences of many orders of magnitude are observed in dilute solutions. In addition, real polymeric liquids show a spectrum of relaxation modes, which can be broken down into a sum of partial stresses:

$$\tau = \sum_i \tau_i \tag{2}$$

Each of the partial stresses τ_i would be described by Equation (1) in the most elementary representation, with a spectrum of material parameters $\{\lambda_i, G_i\}$.

More realistic constitutive equations, some of which are derivable from transient network models (c.f. 4), are of the general form

$$A(\tau_i/G_i) \cdot \frac{\tau_i}{G_i} + \lambda_i \frac{D(\tau_i/G_i)}{Dt} = \lambda_i \left[\nabla v + (\nabla v)^\dagger \right] \tag{3}$$

D/Dt is any properly-invariant derivative, of which the form in Equation (1) is a special case. $A(\tau_i/G_i)$ is a tensor function of the extra-stress, which might involve one or more additional material parameters. The material parameters $\{\lambda_i, G_i\}$ are typically functions of an internal structural parameter (sometimes interpreted as representing the degree of entanglement or the local microstructure), which itself evolves according to a kinetic equation, and the temperature dependence of material parameters must be included for application to practical processing problems.

The Maxwell liquid can be represented alternatively as an integral over the past history of deformation, as follows:

$$\tau = G \int_{-\infty}^{t} \frac{1}{\lambda} \exp\left[(t'-t)/\lambda\right] \left[C^{-1}(t,t') - I \right] dt' \tag{4}$$

C^{-1} is the Finger strain tensor. Integral constitutive equations which capture the important physics are typically of the "Kaye-BKZ" form,

$$\tau = \int_{-\infty}^{t} \left[2 \frac{\partial u}{\partial I_1} C^{-1}(t,t') - 2 \frac{\partial u}{\partial I_2} C(t,t') \right] dt' \tag{5}$$

where u is a strain energy function that depends on $t-t'$ and the first and second invariants (I_1 and I_2) of C^{-1}. There is usually not a one-to-one equivalence between integral and differential constitutive equations.

Many of the polymers of current interest for possible high-performance applications have rigid elements in the molecular backbone, and stress constitutive equations developed for flexible polymers are not applicable. The rigid molecular systems are usually liquid crystalline, with a "domain"-like microstructure in the liquid state that persists over a micron length scale. The Leslie-Ericksen continuum theory (5) developed for monomeric liquid crystals may describe some of the mechanical responses of these rigid-rod polymers, as may the Doi theory of liquid crystalline polymers (2), but both have serious deficiencies; the Leslie-Ericksen theory was not developed for macromolecules, and cannot account for phenomena such as the observed creep in nematic elastic stresses (6), while the Doi theory does not include these elastic stress terms at all. Neither theory can apparently account for the observed "domain" structure in the melt.

NUMERICS AND SINGULARITIES

The numerical solution of flow problems in complex geometries with stress constitutive equations like those listed above has been a major topic of study for the last decade, and has been the subject of five international workshops, the proceedings of which have been published as special issues of *J. Non-Newtonian Fluid Mechanics*. The topic is the subject of other papers in this symposium, and the state of the art is summarized in the comprehensive review by Keunings (7). Successful numerical simulation of flow in complex geometries has been elusive, apparently because of the propagation of exceedingly large stresses that are generated near corners and lips. The nature of the singularity for viscoelastic liquids near a confined corner or lip is unknown, and it is therefore not possible to evaluate calculations of velocity fields and stress growth near corners. Solution of the singularity for Equation (1) and its generalizations would be a major contribution to the understanding of processing fluid mechanics, and could lead to major advances in the simulation of processing flows. A rough estimate (8) based on a limiting case suggests that the stresses generated in a finite region near a corner or a lip could exceed the adhesive strength between the polymeric liquid and the metal die, and even the ultimate strength of the liquid, unless the no-slip condition is relaxed.

ADHESION BOUNDARY CONDITION

The no-slip boundary condition has been a fundamental tenet of classical fluid mechanics for more than a century. There is growing evidence to suggest that this boundary condition is inappropriate for the flow of polymer melts. The most dramatic manifestation of failure of the no-slip condition under processing conditions is contained in Ramamurthy's experiments (9), which demonstrate that the onset of a flow instability in extrusion can be delayed by changing the materials of construction of the metal die. The correct melt/metal boundary condition is not known, but there appears to be a region beyond a critical stress in which the slip velocity is linear in the wall stress (10). The continuum boundary condition at a solid surface is probably related to conformational changes in the polymer chain caused by the presence of the surface, by adsorption, and perhaps by chemical reaction. Determination of this interaction will have far-reaching consequences, which of course include enhanced ability to compute stress and velocity distributions in processing flows.

FLOW INSTABILITIES

Polymer processing operations are often limited by the onset of flow instabilities. Extrudate surface distortion, known as "sharkskin" or "melt fracture", has been the subject of numerous hydrodynamic stability analyses using viscoelastic constitutive equations (e.g., 11,12,13); a flow instability in simple shear at low Reynolds number has never been established, however, when the no-slip boundary condition is implemented. A stability analysis by Pearson and Petrie (14) which is based on introduction of a wall slip law does predict one set of stability experiments nicely (10), but the predicted wave form is not that observed experimentally. Low Reynolds number instability of viscoelastic liquids remains an open and challenging question.

The stability of the interface between immiscible polymeric liquids in coprocessing operations (co-extrusion, co-molding, etc.) is an important question that has received little attention. Free surface instabilities in flows for which thin-sheet and thin-filament approximations are appropriate, such as fiber spinning and film blowing, are understood at least in qualitative terms (15,16,17,18).

Processing flows often involve deformation and shaping of anisotropic liquids, particularly liquid crystalline polymers and fiber-filled composites. These materials are characterized in flow by coordinated motions of rigid elements, either microscopically in the polymer backbone or in the form of macroscopic fibers. We have already noted that the Leslie-Ericksen theory for nematic liquid crystals is probably not appropriate for the flow of polymeric liquid crystals. The mechanics of Leslie-Ericksen liquids has been studied in only the simplest flows, and solutions for converging flow have only just been obtained (19). These fluids contain orientation boundary layers that are induced by wall ordering and elastic stresses, and for certain values of rheological parameters "tumbling" flows can exist.

A complete continuum theory exists for non-interacting suspensions of rigid fibers (20,21), and the theory is in good agreement with flow experiments in a contraction. Large qualitative differences relative to the flow of the unfilled suspending fluid are predicted and observed at fiber loadings as small as 0.1 percent. There is no continuum theory available for the concentrated fiber systems of interest in real composite processing applications, however, and it is clear that the theory for dilute fiber suspensions is inappropriate because of the neglect of coordinated motions. It is likely that some insight is available through solution of the Leslie-Ericksen equations for monomeric nematic liquid crystals, despite the fact that the elastic stresses resulting from the interactions of rigid particles in a liquid crystal have a thermodynamic basis that is absent in the fiber-filled systems.

ACKNOWLEDGMENT

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