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Simulation of Polymer Melt Processing

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Polymer melt processing requires an integration of fluid mechanics and heat transfer, with unique issues regarding boundary conditions, phase change, stability and sensitivity, and melt rheology. Simulation has been useful in industrial melt processing applications. This brief overview is a personal perspective on some of the issues that arise and how they have been addressed. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1641–1647, 2009
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Introduction

Polymeric materials are used in the solid state, but much of the processing occurs as a liquid melt: rods are extruded, molds are filled, fibers and films are drawn, etc. It is during the melt shaping process that polymer chain orientation is effected, and chain orientation greatly influences the subsequent solid morphology and physical properties.

Polymer melt processing requires an integration of fluid mechanics and heat transfer. The liquids are typically viscoelastic; i.e., the stress depends not only on the current rate of deformation, as with low molar mass liquids, but also on the deformation history, sometimes over time scales that are greater than the residence time of the melt in the processing geometry. Viscous dissipation can be important. The boundary conditions at the high stress levels experienced by these very viscous liquids sometimes seem to deviate from the ''no-slip'' condition of classical fluid mechanics. Fluid elasticity is the apparent cause of flow instabilities that do not occur in low molar mass liquids under similar flow conditions. Solidification, either through a glass transition or crystallization, may occur in the processing geometry.

The simulation of polymer melt processing operations for engineering purposes has been an active field for more than 40 years, with important early books by McKelvey,[1] Pearson,[2] and Tadmor and Klein,[3] and the field has progressed in tandem with advances in polymer melt rheology and computing power. There is a comprehensive treatment in our recent text,[4] where detailed references may be found. The purpose of this brief review is to give a personal perspective on some of the issues that arise in the processing of unfilled thermoplastics and how they have been addressed.

Polymer Rheology

The most basic rheological measurement is linear viscoelasticity, which is nothing more than classical frequency response analysis: the melt is subjected to a small mechanical disturbance in shear stress (τ) or shear strain (γ) that probes all accessible dynamical modes, usually in the form of sinusoids or sums of sinusoids, and the output is monitored. The most common approach is to represent the shear stress as a sum of partial stresses, $\tau = \sum \tau_n$, where each partial stress is represented by a first-order linear dynamical system:

$$\lambda_n \frac{d\tau_n}{dt} + \tau_n = \lambda_n G_n \frac{d\gamma}{dt} \qquad (1)$$

The distribution of relaxation times $\{\lambda_n\}$ and moduli $\{G_n\}$ defines the small-amplitude dynamical response. It is straightforward to show that the zero-shear viscosity $\eta_0 = \sum \lambda_n G_n$.

The generalization of the one-dimensional linear description to describe three-dimensional finite motions is not straightforward. While finite deformation empiricisms have long been in use, current practice is to use continuum stress constitutive equations that are derived from one of two theoretical approaches:

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The *temporary network* approach is a generalization of the theory of rubber elasticity, and it leads to equations of the form $\boldsymbol{\tau} = \sum \boldsymbol{\tau}_n$, where each partial stress usually satisfies a differential equation of the general form

$$\lambda_n \left[\frac{\partial \boldsymbol{\tau}_n}{\partial t} + \mathbf{v} \cdot \nabla \boldsymbol{\tau}_n - \nabla \mathbf{v}^T \cdot \boldsymbol{\tau}_n - \boldsymbol{\tau}_n \cdot \nabla \mathbf{v} + \boldsymbol{\varphi}_{\mathrm{n}}(\boldsymbol{\tau}_n, \nabla \mathbf{v}) \right] + \mathrm{Y}_{\mathrm{n}}(\boldsymbol{\tau}_{\mathrm{n}})\boldsymbol{\tau}_{\mathrm{n}} = \lambda_n G_n (\nabla \mathbf{v} + \nabla \mathbf{v}^T), \qquad (2)$$

where $\mathbf{v}$ is the velocity vector. The functions $\boldsymbol{\varphi}$ and Y depend on the particular assumptions in the derivation; $\boldsymbol{\varphi}$ is always a sum of inner products of one or both of its arguments. Each function contains one parameter; hence, in addition to the linear viscoelastic spectrum $\{\lambda_n, G_n\}$, there are two nonlinear parameters that must be obtained for each dynamical mode. The basic idea of the temporary network goes back more than 40 years to work by Green and Tobolsky, Lodge, and Yamamoto; a development of a general framework leading to several constitutive equations that have been used for simulations, together with references to the earlier literature, can be found in Mewis and Denn.[5]

The *tube* approach, which follows the ideas developed by Edwards, De Gennes, and Doi, starts with the observation that any chain in an entangled polymer melt is constrained in its transverse motion by the surrounding chains; hence, the primary chain motion must be in the direction along the chain backbone (*reptation*). This leads to the notion of an effective *tube* through which the chain moves, and this construct, with major subsequent additions by Doi, Marrucci, and others regarding tube motion and the formation and loss of entanglements and the consequent effect on the tube, leads to a class of continuum constitutive equations that incorporate a great deal of molecular information. The constitutive formulations often retain the general structure of Eq. 2, but with more complex nonlinearities. There is a broad review of tube models in McLeish[6] and a more recent review specific to linear viscoelasticity in van Ruymbeke et al.[7]; our own modest contribution to tube theories through a stochastic simulation that incorporates the dynamics of the chain and the tube is in Xu et al.[8]

The mathematical structure of Eq. 2 leads to major computational issues that have only partly been resolved, mainly having to do with very large stress gradients that cannot be resolved numerically. Meaningful computation can be carried out for many processing flows, however, and commercial codes for the solution of flow problems of viscoelastic liquids typically contain both network and tube models. One nice example of simulation of a polyethylene melt through a contraction using both network and tube models, together with birefringence data showing principle stress contours, is in Veerbeeten et al.[9]

Wall Slip

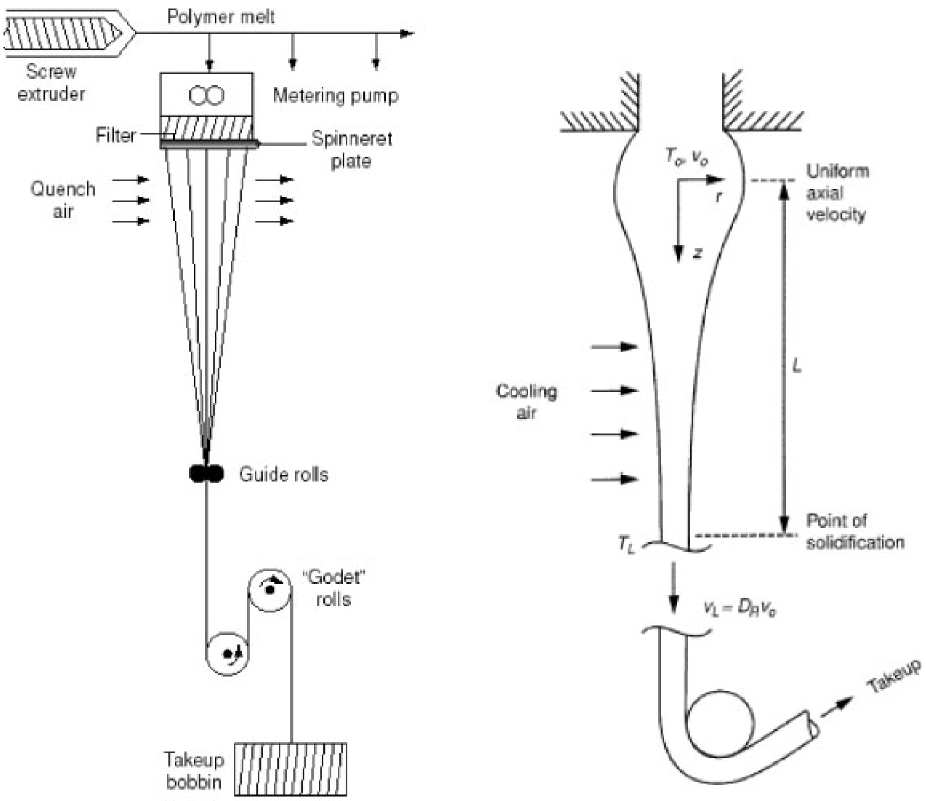
Entangled polymer melts frequently show systematic deviation from the no-slip boundary condition at high stresses. The subject is broadly reviewed by Denn,[4,10] and a recent paper by Park et al.[11] contains informative experiments and more recent references. There is a general consensus that the first measurable onset of apparent wall slip is caused by network failure or disentanglement of chains near the wall (which are equivalent concepts, depending on whether a network or tube approach is used); this results in a wall region made up of more mobile chains, hence a lower viscosity in the wall region relative to the bulk and the appearance of slip. The mechanism has been quantified in a number of studies in the context of the tube approach, most recently in a stochastic simulation that incorporates detailed chain behavior (Xu et al.[12]). Visualization on the length scale of the wall region is very difficult, but the several disentanglement calculations are consistent with limited data.

It is straightforward in principle to incorporate a slip velocity into processing simulations, but detailed data are too limited to have resulted in a universal model to replace the no-slip condition. It is customary to assume that the slip velocity has a power-law dependence on the local shear stress, often linear for convenience (following a 185-year-old suggestion of Navier), although some authors have used slip velocity functions with a maximum and minimum to reproduce the periodic "spurt" flow that is observed in the extrusion of some linear polymers. Slip can have a major effect on the flow pattern of a shear-thinning liquid in a changing cross-section (Joshi and Denn[13]), where the wall shear stress changes considerably with position; this phenomenon might be important in the initiation of flow instabilities that are thought to be associated with curved streamlines in viscoelastic liquids, but it has received little attention.

Thermal Effects

Polymer melts are usually very viscous, they tend to be poor conductors, and they typically have viscosities that are strongly temperature dependent. These factors combine to make viscous heating and heat transfer the dominant factors in many processes, with large localized temperature increases because of viscous dissipation that cannot be conducted away to boundaries. Hence, flow processes like extrusion rarely attain a fully developed temperature profile. Small uncertainties in heat transfer characteristics can mask the effect of complex rheology, although the effect of rheology has received far more attention in the literature. (This point is addressed in the context of model validation for the melt spinning process and the "simplicity paradox" by Denn.[14]) Given this sensitivity, it is surprising how little heat transfer data are available in the open literature for the flow of polymer melts in channels.

Flow in a straight conduit illustrates the importance of thermal effects, and informative results of processing significance can be obtained analytically by considering cross-sectional averages of the governing momentum and energy equations. One case of interest is flow at a very high pressure drop, such as might be encountered in injection molding; here, the effect of the very slight compressibility of the melt on the viscosity through free-volume effects must be taken into account. The pressure drop will increase without bound at a finite throughput ("choking") if isothermal flow can be maintained. Viscous dissipation will cause the pressure to pass through a maximum with increasing flow rate and then decrease, however, and it is for this reason that choking is not observed in practice (Denn[15]; subsequent references are in Denn[4]).



(a) (b)

Figure 1. (a) Overall schematic of the melt spinning process; (b) schematic of a single filament.

Another striking example of the significance of thermal effects is found in developing flow in a channel with wall heat transfer, which was first analyzed by Pearson et al.[16] and is treated in a slightly different manner by Denn.[4] Here, the effect of pressure on the viscosity has not been considered. The dimensionless pressure drop can exhibit a maximum and a subsequent minimum as a function of dimensionless throughput, indicating multiple flow rates for a given pressure drop. A discontinuous jump from a slow-flow to a high-flow steady state is thus expected with increasing pressure drop, with hysteresis in the reverse direction. (The intermediate solution is unstable.) The situation is analogous to the ignition/extinction transition in combustion and the discontinuous transition between low temperature-low conversion and high temperature-high conversion steady states in continuous flow reactors and catalyst particles (*cf.* Denn[17]). The effect of a pressure-dependent viscosity on this phenomenon is not known.

Nearly all published analyses of nonisothermal flows of polymer melts use a form of the energy equation that implicitly assumes that the contribution of the orientation of the polymer chains to the free energy is strictly entropic, and nonisothermal stress constitutive equations that assume the applicability of time–temperature superposition, wherein the only effect of temperature is to change the time scale of viscoelastic response. Experiments by Matsumoto and Bogue[18] on nonisothermal stretching seem to exhibit heating rates that are inconsistent with the equations that derive from these assumptions. The proper formulation of stress and energy equations for polymeric liquids is broadly addressed by Dressler et al.,[19] but there has been very little practical attention to this issue, which could be quite important in the presence of large temperature gradients, and current practice is to use equations derived from the "standard" assumptions.

Melt Spinning

The melt spinning process for the manufacture of textile fibers has been studied extensively and is a good example of how simulation can be used to guide process design and operation. The melt spinning process is shown schematically in Figure 1. The individual fiber in a fiber bundle is extruded as a melt through a small *spinneret* hole into ambient air and drawn down by a takeup roll moving at a linear velocity that is much higher than the mean extrusion velocity. Solidification occurs before takeup. The takeup speed can exceed 5000 m/min, so inertia and aerodynamic effects are important, and the residence time in the melt phase may be much shorter than the characteristic stress relaxation time of the liquid. The analysis is usually carried out using *thin filament equations* that exploit the very different length scales in the transverse and draw ("machine") directions.

Analyses of melt spinning were done independently by Kase and Matsuo[20] and Matovich and Pearson,[21] building on earlier work of Ziabicki that is cited in a comprehensive monograph[22] that is now dated. Kase's model formed the basis for an in-house Toyobo company code to simulate poly(ethylene terephthalate) (PET) spinning that included methods of accounting for multiple fibers; Kase's code was commercialized by Toyobo, and similar in-house codes were developed and used for single and multiple fibers by other fiber producers. The first viscoelastic analysis was reported in an unpublished MChE thesis by Zeichner,[23] and the first full viscoelastic treatment was published by Denn et al.[24] for isothermal operation and by Fisher and Denn[25] for nonisothermal operation. There is a comprehensive review of spinning models through 1983 by Denn[26] that includes comparisons with pilot-scale data, and more detailed derivations and recent studies are described by Denn.[4]

The thin filament model does a good qualitative job of describing steady spinning of PET at low to moderate takeup speeds. The major modeling issues have to do with the sensitivity to two transport coefficients that are exceedingly difficult to measure in independent experiments, namely the drag coefficient and the heat transfer coefficient, and a good understanding of these coefficients even for single filaments remains elusive (Denn[27]). The fixed-temperature solidification condition seems to have been the reason for failure of these models when applied to high-speed spinning (>4000 m/min) of PET, in which there is rapid solidification to a high crystal fraction and the formation of a neck; steady high-speed spinning of crystallizable polymers was successfully addressed in a series of articles by McHugh and coworkers (see Shrikhande et al.[28]), who included the dynamics of stress-induced crystallization and a mixing model for the stress that incorporates the contributions of both the liquid and the crystalline phases.

Steady spinline models have been extremely useful in industrial applications, despite the uncertainty in essential transport parameters and the difficulty posed by the solidification condition. The best use has been as a guide for the design of quench air systems, where the models show the effect of air distribution on the development of the stress. The concepts behind a series of commercialized patents by Vassilatos and coworkers (e.g., Vassilatos,[29] Sweet and Vassilatos,[30] Nguyen et al.[31]) on quench air systems for high-speed spinning of PET, collectively known as pneumatic spinning, were initially developed using a spinline model; the technology enabled high throughput production of noncrystalline PET yarns with improved uniformity at speeds at which stress-induced crystallization usually occurs.

Stability and Sensitivity

The dynamical response of melt spinning is perhaps the most studied of all transients in polymer processing operations, because in large measure, the thin filament equations are sufficiently simple that the conventional stability and sensitivity analyses used in reactor analysis and control theory (e.g., Denn[17,32]) can be applied.

An instability known as draw resonance, or melt resonance, which causes periodic variations in coating thickness that degrade the optical properties of extrusion-coated sheets, is also observed in spinning; spinning is easier to study in the laboratory than extrusion coating, hence draw resonance in spinning has received considerable attention. Spinline draw resonance is characterized by a periodic variation in fiber diameter at constant extrusion and takeup speeds. The name arose because of a presumption that the oscillations were driven by a resonant response of a dynamical mode associated with the viscoelastic time scale of the polymer, but this presumption is not correct; draw resonance is observed in Newtonian liquids,[33] and the oscillation period is associated with the residence time in the melt zone of the spinline. The first theoretical studies of draw resonance were carried out independently by Kase et al.[34] and Pearson and Matovich[35] for inelastic liquids, and subsequently by Fisher and Denn[25,36] for viscoelastic liquids. The early literature is reviewed by Petrie and Denn[37] and, successively, by Denn.[4,26,38] Briefly, for a fixed spinning length and isothermal conditions, a Newtonian fluid spinline exhibits draw resonance at a drawdown (area reduction) ratio of 20.2; extension thinning, or decrease in the extensional viscosity with increasing stretch rate, is destabilizing (lower critical drawdown ratio), while viscoelasticity, heat transfer to the surroundings, and dynamical adjustment of the solidification point are stabilizing. Draw resonance is rarely, if ever, observed in commercial melt spinning of PET and nylon because of the large temperature gradients in the spinning direction and the natural dynamical adjustment of the freeze point. There are reports of draw resonance in the spinning of some polypropylenes, possibly because the high degree of extension thinning overcomes the stabilizing effects of cooling and freeze point adjustment. [The solution spinning process for the production of fibers from the liquid crystalline polymer poly(*p*-phenylene terephthalamide), produced commercially as Kevlar® and Twaron®, consists of a nearly isothermal zone followed by a fixed quench location, after which the solvent is removed; draw resonance is to be expected for this process, but there have been no published reports.]

In contrast, dynamical *sensitivity* of a spinline, which investigates the attenuation and amplification of disturbances, is of considerable commercial importance. (There has been some confusion in the literature about the distinction between draw resonance and dynamical sensitivity, with the unfortunate publication of some utter nonsense that will not be cited here.) Traditional frequency response techniques can be used to study sensitivity; there are control theoretic approaches by Kase and Denn[39] and Denn,[32] and a detailed frequency response analysis of nonisothermal spinning of viscoelastic liquids is developed by Devereux and Denn.[40] One conclusion that is readily reached is that fluctuations in heat transfer to the cross-flow air are the only disturbances that are amplified in a relevant frequency range, and these must be the primary source of diameter fluctuations in the drawn filament. We are aware of only a single quantitative data set to test spinline frequency response calculations, by Young and Denn.[41] Devereux and Denn[40] obtained acceptable agreement between their frequency response calculations and Young and Denn's[41] experiments on the sensitivity of a PET spinline to cross-flow air fluctuations, but they found very poor agreement with the experiments on the sensitivity of polypropylene, which is a crystallizing polymer. Their conclusion was that a better treatment of the dynamical response of the solidification region, and a better understanding of the solidification process in general, was essential for

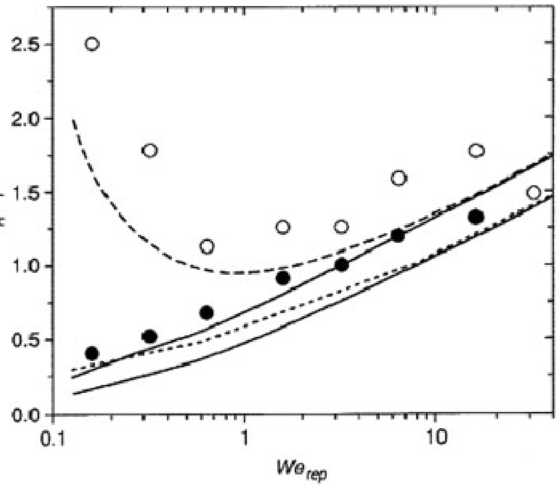


Figure 2. Total strain (ε_T, open symbols) and recoverable strain (ε_R, filled symbols) at failure as functions of dimensionless stretch rate (We_{rep}) for uniaxial stretching of a narrow-distribution polyisoprene melt (data of Vinogradov), together with the calculations from the scaling analysis (solid lines are recoverable strain, broken lines are total strain).

The lower lines are obtained with a scaling coefficient of unity, whereas the upper lines are obtained with a scaling coefficient of 2.5. (From Joshi and Denn *J Rheology*. 2004;48:591–598.)

the simulation of crystallizing polymers. Kohler and McHugh[42] repeated the frequency response analysis using a stress-induced crystallization model for solidification, and they claimed better agreement with the experiments, but it is our opinion that there is no marked improvement for the polypropylene (*cf.* Denn[4]). Incorporation of crystallization kinetics and the influence of the crystal phase on the mechanics are clearly important, but we believe that the dynamical treatment of crystallizing polymers remains an open issue.

Failure

Failure is the primary dynamical problem in commercial fiber spinning, and it is unlikely to be related to the instability and sensitivity mechanisms discussed earlier. Polymer melt filaments fail through capillary, ductile (necking), and cohesive mechanisms, depending on the stretch rates. Capillary failure of viscoelastic liquids is most important for low viscosity polymer solutions, where surface tension-driven breakup may be delayed relative to Newtonian liquids by the formation of a persistent "bead-on-a-string" morphology, which is understood mechanistically (Bousfield et al.[43]). It is cohesive failure that is the most intriguing and elusive, because it is difficult to conceptualize the mechanism of a brittle solid-like failure in a polymeric liquid. The search for a mechanism for brittle failure in liquids dates at least to work by Reiner and Freudenthal[44] and is discussed in reviews by Petrie and Denn,[37] Malkin and Petrie,[45] and Joshi and Denn.[46] Joshi and Denn[47] used what might be best described as a caricature of the tube approach in a simple scaling analysis (quite literally doable on the "back of an envelope") that includes a scaling coefficient of order unity; the analysis does predict failure that is in agreement with very limited quantitative data on narrow-distribution polymer melts (see Figure 2). Within the context of the analysis the failure would seem to be associated with a chain pullout mechanism, but there is no realistic molecular-level physics in the treatment and a good theoretical understanding is still missing. (Spinline failure for PET is probably caused in most cases by the presence of trace amounts of cross-linked gel particles, which cause a local stress concentration leading to extensional failure. It would be difficult to quantify this phenomenon even with a good theory for extensional failure.)

Sharkskin, an instability that arises during the extrusion of some linear polymer melts wherein a small-amplitude, high-frequency disturbance appears on the extrudate surface (see Figure 3[48]), is almost certainly caused by an extensional failure at the point where the melt exits the extrusion die. (This mechanism was first suggested by Cogswell[49] and has been a point of contention in the literature for decades, but the experimental evidence now seems convincing; see references in Denn.[4]) The scaling approach used by Joshi and Denn[47] is insufficient to explain this failure, which involves not only a rupture because of large tensile stresses at the point of departure, but also penetration of the tear into the bulk and the creation of new interfacial area, followed by stress release and healing. Hence, while the mechanism is understood in broad terms, a quantitative description with predictive ability is missing and will require going beyond the simple failure mechanism in extension.

Boundary Condition at Infinity

One of the intriguing and often neglected aspects of the flow of polymer melts is the subtle effect of boundary conditions. In rheometry, for example, shear and normal stresses

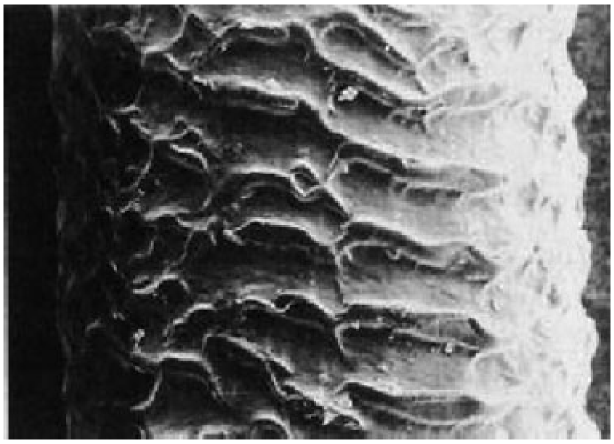


Figure 3. Extrudate of linear low-density polyethylene exhibiting sharkskin.

(From Pudjijanto and Denn *J Rheology*. 1994;38:1735–1744.)

are often measured using a cone-and-plate device with a small cone angle, because the shear rate is nearly constant throughout the gap. The theory for the rheometer requires the dynamic pressure, which must be obtained for an incompressible liquid through balancing the normal stress at a free surface against the atmosphere. The momentum equation is satisfied only to within an error of the order of the cone angle, even in the absence of inertia, in the standard analysis of a cone-and-plate rheometer, and this balance holds only if the free surface is the arc of a circle, which it frequently is not. Hence, the cone-and-plate rheometer is subject to interface-induced flow disturbances that might be misinterpreted as novel physical phenomena; an example may be found in Inn et al.[50]

This effect of the ''boundary condition at infinity'' is nicely illustrated in squeezing flow, which is the kinematical basis of the process of compression molding. The issue first arose in an analysis of the compression molding of layered fluids (Lee et al.[51]), simulating a situation where the fluid near the hot plates has a much lower viscosity than the fluid near the center plane; the low viscosity fluid may sometimes encapsulate the core material as the plates close. The standard analysis of this flow, as carried out in classical lubrication theory, would not permit encapsulation because of the way that the base flow is handled as the radial coordinate goes to infinity; more importantly, because of the way in which the pressure is determined, it would lead to a completely incorrect estimate of the compressive force, namely, that the compressive force is determined entirely by the viscosity of the fluid adjacent to the plate, regardless of how high the viscosity of the core fluid may be. The issue is addressed in some detail by Lee et al.,[51] where the issue of boundary conditions is discussed, the mechanism of encapsulation is demonstrated, and the paradoxical force calculation is resolved; see also Denn and Marrucci,[52] where the effect of the finiteness of the plates is addressed. The problem does not arise, of course, for numerical simulations of finite geometries that account properly for the boundary conditions along the external free surface.

Another striking illustration of the dominant effect of the boundary condition at infinity can be found in the development of the temperature profile in a simple model of a single-screw extruder. The balance between drag flow and a pressure-driven backflow requires a transverse velocity component at the channel ends that is (properly) ignored in the standard treatment of the fluid mechanics. The transverse component has a profound effect on the temperature profile across the gap, however, and failure to consider this effect leads to a qualitative difference in the developing temperature profile in the channel.[4]

Finally, polymer processing is usually done at high deformation rates, while the methods for measuring rheological functions other than the shear viscosity are usually restricted to relatively low deformation rates. This dichotomy has led to efforts to make high-rate measurements of the nonlinear stresses normal to the shear direction. One such approach involved measuring the ''exit pressure,'' defined as the difference between atmospheric pressure and the value obtained by extrapolating wall pressure transducer readings to the exit of a capillary or slit extrusion die. This methodology, which was implemented commercially, gave incorrect values for the rheological functions because of a faulty analysis that ignored the rearrangements in flow near the far-field boundary condition, in this case at the exit. (There were also problems in measuring the ''exit pressure,'' but the problem with the analysis was fatal in any case.) A full treatment of this type of measurement for both melts and solutions is given by Boger and Denn.[53]

Concluding Remarks

The issues addressed here are among the major ones that arise in the simulation of polymer melt processes; the scope of processes is of course much wider, but the essential issues—boundary conditions, heat transfer, phase change, stability, sensitivity, rheology—are always present and will remain active areas for research. Rheology tends to receive the most attention in the research literature, but in many cases it is not the most important factor in developing a useful model for a process.

Acknowledgments

I am grateful to Stanley Sandler for having inviting me to write this personal overview of a field with which I have been involved for most of my professional career, and it is especially gratifying that it will appear in a journal of which I was the Editor some 20 years ago. The PhD students, postdocs, and professional colleagues with whom I worked on issues related to polymer processing, and who were the major contributors to most of our joint studies, are too many to mention individually, but they appear as co-authors on publications cited here and, to a much greater extent, in Denn.[4] Polymer processing is of little significance as an area of academic study without a strong connection to the polymer industry, and I want to make special mention of three outstanding industrial colleagues, George Vassilatos, Kurt Wissbrun, and A. V. Ramamurthy, who generously shared their knowledge with me and with the broader academic community. The late Arthur B. Metzner was my mentor and my colleague during my years at Delaware, and he had a major influence on my work.

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