POLYMER FLOW INSTABILITIES
A Picaresque Tale

The thirty-first annual Chemical Engineering Division Lectureship Award was presented to Morton M. Denn at the June, 1993, annual meeting of ASEE held at the University of Illinois, Urbana-Champaign, Illinois, for his lecture (presented here) titled "Polymer Flow Instabilities: A Picaresque Tale." The purpose of this annual award is to recognize and encourage outstanding achievement in an important field of fundamental chemical engineering theory or practice.

Morton Denn is Professor and Chairman of Chemical Engineering at the University of California at Berkeley. He earned his BSE from Princeton University in 1961 and his PhD from the University of Minnesota in 1964. After spending a post-doctoral year at the University of Delaware he joined the Delaware faculty, where he was named the Allan P. Colburn Professor in 1977. He went to Berkeley in 1981, where he also serves as Program Leader for Polymers and Composites in the Center for Advanced Materials of the Lawrence Berkeley Laboratory.

Denn's PhD dissertation with Rutherford Aris, The Optimization of Complex Processes, was the start of an interest in process optimization and control that lasted for many years; the fruits of this period include his text Optimization by Variational Methods (1968). His postdoctoral work with Arthur B. Metzner on rheology and non-Newtonian fluid mechanics defined the other major focus of his research interests. This work has included theoretical and experimental rheology of polymer solutions and melts and analytical, computational, and experimental investigations of the flow of complex liquids. Flow instabilities have been a particular concern.

Much of Denn's research has focused on modeling the steady and dynamical behavior of processing operations. These activities are illustrated in his book Process Modeling (1986).

Denn's interest in education is reflected in his textbooks, which in addition to those noted above include Introduction to Chemical Engineering Analysis (with T.W.F. Russell, 1972), Stability of Reaction and Transport Processes (1975), and Process Fluid Mechanics (1980). His professional activities include service as Editor of AIChE Journal from 1985 to 1991.

Denn is a member of the National Academy of Engineering and a Fellow of the AIChE. He was a Guggenheim Fellow and a Fulbright Lecturer and has received the Bingham Medal of the Society of Rheology and the Professional Progress and William H. Walker Awards of the AIChE.

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I am honored to have been chosen to deliver the 1993 ASEE Chemical Engineering Division Lecture. While this brief written text cannot capture the mood of an hour-long evening presentation to a relaxed and friendly group, I hope it does convey some of my excitement over the topic.

Extrusion instabilities are ubiquitous in polymer processing and have commanded attention for four decades; my students and I have been studying them off and on for nearly three, and the entire time has been a learning experience. I chose this subject for my lecture because I believe the path which has been followed mirrors the evolution of chemical engineering research over the same time period; we have moved from the macroscopic to the molecular level as finer-scale tools, experimental and theoretical, have become available. This has not happened because the nature of the problems has changed, but rather because we are better equipped to deal with them on a fundamental level. I have commented elsewhere on the risks to the soul of our profession which are inherent in too strong a research emphasis on the underlying sciences; here I will look only at the gains.

I subtitled my lecture "a picaresque tale," which I find descriptive of the progression of our focus from millimeter-sized dies to molecules. The scoundrels along the way have only sometimes been evident, and on rare occasions the quixotic has been clouded by the appearance of epic triumphs; in every case (save the current one, which is still in doubt) the Homeric landscape has faded and the windmills have reappeared. The physical phenomenon being studied is deceptively simple. Beyond some critical throughput in an extrusion die, all polymer melts develop irregularities on the surface of the extrudate, sometimes accompanied by unsteady flow in the die. Polymer melts are viscoelastic, and the simplest description of the stress state requires at least two material parameters: a modulus
and a viscosity. The modulus, which is typically of order 0.1 MPa, can be estimated from a variety of measurements with varying degrees of rigor. A useful empiricism is that the first visual onset of surface irregularities occurs when the wall shear stress is comparable to the modulus. (The ratio of stress to modulus is often called the recoverable shear.) The empiricism is not surprising; in the absence of inertia, which is always the case in melt extrusion, and with the dubious assumption of fully developed flow everywhere in the die, the critical velocity might be expected to depend primarily on the viscosity, the die diameter, and the modulus—in which case the idea of a critical recoverable shear follows immediately from dimensional analysis.

In linear polyolefins the first visual manifestation of an extrusion instability is a high-frequency, small-amplitude distortion known as sharkskin (Figure 1). The onset of sharkskin appears to coincide with a change in the slope of the flow curve (shear stress vs. shear rate). In constant throughput processing (as opposed to constant pressure drop or, equivalently, constant stress) there is a second critical stress at which pressure and flow rate oscillations\(^*\) occur and the extrudate emerges with alternating "sharkskinned" and relatively smooth sections (Figure 2). This regime is known as slip-stick.

Finally, at still higher throughput, pressure oscillations cease, sharkskin vanishes completely, and there is a transition to a wavy distortion which gradually becomes more severe. A typical flow curve is shown in Figure 3, where the slip-stick region is reminiscent of ignition-extinction phenomena in combustion; in constant pressure operation the intermediate portion of the curve is unattainable and there are hysteretic jumps between the two branches. The slipstick discontinuity is absent in other polymers, such as branched polyolefins and polystyrene, and the first instability is often more pronounced than sharkskin. These instabilities are often known collectively as melt fracture, a term coined in 1956 by Tordella because he heard crackling noises in the die and the extrudate had the appearance of a fractured solid material. Elastic turbulence is another common early term which has now largely disappeared.

Flow instabilities in viscoelastic liquids have been the subject of several major reviews (see, for example, Petrie

\* Flow rate oscillations are possible in constant throughput operation because of the small degree of compressibility of the polymer melt.
and Denni[2] and Larson[33]. I have recently addressed[4,5] what I consider to be the outstanding issues of the subject at hand, and my treatment here will be selective, rather personal, and without references. I do call attention to an excellent set of data on well-characterized polybutadienes and polyisoprenes by Vinogradov and coworkers,[6] which illustrate the phenomena very well and have been used to test several theoretical formulations.

CONSTITUTIVE INSTABILITIES

In 1966 Huseby showed that a molecular theory of polymer melt rheology could lead to a maximum and minimum in the flow curve, reminiscent of the shape in Figure 3, and he suggested that melt fracture is a consequence of the intrinsic rheology. The "reptation" theory of polymer chain motion of De Gennes and Doi and Edwards leads naturally to a flow curve with a maximum, and the subsequent minimum may occur because of rapid molecular motions not contained in the basic theory. The magnitude of the discontinuity in the flow curve in Vinogradov's data has been predicted quite well from this theory by McLeish and Ball; Malkus, Kolka, and their coworkers have explored the rich dynamics of such systems.

This constitutive mechanism does not require molecular theories. The possibility of maxima and minima in flow curves was apparently first noted by Oldroyd in 1950 in the context of a rigorous formulation of continuum theories. Oldroyd considered such behavior unphysical, and I tend to agree. Gabriel Pomar, working with me and Susan Muller, has recently shown that the discontinuity in the flow curve for a series of octadecane-diluted linear polyethylene occurs at a constant stress, independent of modulus, which appears to be inconsistent with the concept of a constitutive instability.

HYDRODYNAMIC INSTABILITY

The appearance of a highly structured distortion suggests the use of hydrodynamic stability theory to explain the behavior. My students and I, as well as a number of others, explored this avenue. In 1973 we succeeded in "predicting" the onset of melt fracture in capillary dies with remarkable accuracy, and we made an experimentally testable prediction for slit dies which motivated at least three experimental studies. The prediction for slits was incorrect, leading to a reexamination of the theory with Teh Ho and the discovery that the eigenvalue problem is so computationally sensitive that false neutral stability curves are the rule. While this was a triumph of the scientific method, it was a great disappointment regarding our understanding of the phenomena and showed (as has been verified by several research groups since) that fully-developed channel flow of model viscoelastic liquids with monotonic stress curves is stable to small disturbances. (I often wonder how a young faculty member subject to today's critical mode of tenure evaluation would fare in such a situation.)

There is no universally accepted equation relating the stress to the strain rate in polymeric liquids, but certain mathematical structures appear in many constitutive formulations. It is a common feature that the full system of equations describing flow can change type; i.e., in certain regions of the flow field they will be elliptic, while in others they will be hyperbolic. (Non-zero inertial terms are required for this change of type.) Hyperbolic equations admit discontinuities, and they allow small boundary disturbances to grow as "Hadamard instabilities." A critical transition of this type has been suggested by Joseph and his coworkers as a mechanism for extrusion instabilities as well as a number of other phenomena.

The first analysis of change of type for viscoelastic liquids was apparently done by my student Jim Ultman in the early 1970s to explain anomalous heat transfer in dilute polymer solutions, so I have a certain fondness for this approach, but I doubt its general applicability. The notion of change of type is inconsistent with explanations based on a constitutive instability.

WALL EFFECTS

The standard macroscopic tools which we used in the sixties and seventies (rheological measurement and continuum mechanics and stability theory) provided little insight into the problem of extrusion instabilities, and flow experiments were not instructive regarding mechanisms. A dramatic turn came with the publication of a paper by Ramamurthy in 1986 in which he demonstrated that the stress for the onset of extrudate distortion in an alpha-brass die was different from one made of chrome-plated steel. (Similar observations had been made twenty years before, but had attracted little attention.) Rather than serving as a passive element, with the sole function of providing an anchor for a no-slip condition, the die wall was shown to be an active element in the process.

Exploration of the limits of the no-slip condition is not new—I recall writing a course paper reviewing some of the literature when I was in graduate school—but the notion that wall effects could influence liquid-phase processing seemed revolutionary. Measurements in our laboratory by Doug Kalika were consistent with the observation that the onset of sharkskin in linear low-density polyethylene coincides with the onset of apparent wall slip. Glenn Lipscomb, Roland Keunings, and I estimated the stresses at a corner in the flow (using a most inexact theory for a problem that is still unsolved for any stress constitutive equation of interest) and found that, while the region over which a Newtonian fluid experiences stresses that exceed the cohesive strength of materials is of atomic scale, for polymer melts the region is of the order of tens of microns, casting doubt on the applicability of the no-slip condition near boundary discontinuities.
Davide Hill, Tomichi Hasegawa, and I showed in 1990 that the theory of the adhesion of elastomers to rigid substrates could be extended to flowing polymer melts at high levels of stress, and that adhesive failure between the melt and the wall is predicted to occur at stresses quite close to those where sharkskin is observed. Furthermore, the theory provides an a priori calculation of the dependence of the slip velocity on wall stress which is in remarkably good agreement with Kalika's measurements.

What is significant is not the quantitative agreement between theory and experiment, for the theory has important limitations which make it clear that the extent of agreement is fortuitous, and a mechanism for the periodicities characteristic of sharkskin and slip-stick seems to be missing. Rather, the significance is in understanding the instabilities is most likely to be made by applying the tools of surface science and dynamic fracture in place of the macroscopic methodologies which had dominated the field. For me, it meant a major redirection of my research effort.

POLYMER SURFACE PHENOMENA

Once we accept the principle that some flow instabilities are governed by surface effects, molecular probes of the surface become the logical means of study. Let me give two examples here of our recent and ongoing work which reflect this change in methodology.

Our theoretical treatment of adhesion at the melt/die wall interface requires that we understand the adhesion of solid polymers to metals under conditions where the interactions are mostly governed by dispersive forces. In our laboratory, Davide Hill and, more recently, Tim Person have used ion and electron spectroscopies, primarily SIMS and XPS, to study the adhesion of polyethylene at metal and metal-oxide substrates. Following removal of a polymer film from the metal substrates, Hill saw evidence of transfer of metal atoms to the polymer. We find consistently that a 2- to 6-nm layer of polymer is left behind on the metal, although the metal is also clearly revealed, possibly because the crack moves between the phase boundary and the interior of the polymer. Surface chemistry involving the metals under extrusion conditions seems to be very important to the nature of adhesion. The question of whether the failure is adhesive, cohesive, or a mix of the two is important to the theory of melt slip; the energetics leading to agreement with experiments assume adhesive failure, and a cohesive failure would give different results.

Laura Dietsche and, more recently, Christophe David, working with me and Alex Bell, have used attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR) to study the dynamics of chain exchange between the bulk melt and the channel surface in a flow system, working with C-16 oligomers. The dynamics of exchange are complex, with surprisingly long time scales. When the flow channel is filled with one oligomer and displaced with the other, the initial transient response is consistent with simple flow and diffusion. Dietsche found, however, that at a critical surface concentration, which is independent of flow rate but very dependent on the material of construction of the channel face, there is a transition to an apparent first-order process with a time constant of order one minute; the exact time constant is flow rate and surface dependent. The time constant can be lengthened by the addition of chains with functional groups like those used in some commercial "flow modifiers."

The dynamics seem to be governed by a very slow adsorption/desorption process, which probably results from a tendency of chains to extend and densify at the surface, as predicted in somewhat different contexts by several molecular dynamics simulations. This observation is clearly relevant to the behavior of chain segments in an entangled polymer near a surface, but it is possible that entanglement-dominated surface dynamics will be rate-limiting for macro-molecular melts, and the relevance of this fascinating phenomenon to the dynamical processes associated with extrusion instabilities is presently unclear and needs further study.

WINDMILLS?

Following extrusion experiments in our laboratory by Hideo Shidara, using slits as small as 34 µm in height to achieve a large surface-to-volume ratio, I noted an interesting difference between instabilities in linear polyethylene and polystyrene. (As with most important observations, this one was not new; I simply had not appreciated the significance before.) In the region of flow instabilities there was a decrease in the polyethylene extrusion pressure, suggestive of wall slip. With polystyrene, however, the flow became more dissipative following the onset of the instability.

This behavior could be rationalized in the context of an adhesion mechanism, but alternative ideas are possible. It should be much easier, for example, to pull linear polyethylene out into an extended-chain conformation at high stress than the bulky polystyrene, and the possibility of a stress-induced phase change leading to a low-viscosity material near the wall (perhaps a liquid-crystalline phase) had to be considered. Several years ago, Andrew Keller claimed to have observed a liquid-crystalline transition in high-density, high-molecular-weight polyethylene, so the idea had some respectability even if it seemed a bit unlikely.

While pursuing this concept, Stephanus Pudjjianto and I recently showed that a linear low-density polyethylene can exhibit a remarkable "stable island" in the midst of the slip-stick region, where pressure oscillations stop, extrusion pressure drops, and the extrudate becomes reasonably smooth. At throughputs on both sides of this "island," which exists only in a narrow temperature range, unstable oscillating
flow persists. Thus far we have found no evidence of the existence of a liquid-crystalline phase in the near-surface region. This experimental observation does not seem to fit into any of the theoretical frameworks developed thus far for the instabilities, including the surface-dominated mechanism.

EPILOGUE

What started nearly thirty years ago as a classical continuum problem has evolved into a study of molecular interactions at surfaces, in my laboratory (which I have emphasized here) and others. We are following this path because our ability to study real processing problems at a molecular level is enhanced by tools which were previously unknown or unfamiliar to us.

Our goal is unchanged from what it was when we began, but our methodology is quite different. My students are routinely using a variety of surface-sensitive methods (those mentioned above and other microscopies and spectroscopies) to study the mechanics of polymer interfaces, as are those in other laboratories. My colleagues Arup Chakraborty and Doros Theodorou, and their counterparts elsewhere, are using powerful computational and theoretical methods to study polymer chain conformations and dynamics near surfaces because of their own interests in a variety of practical problems.

I believe a thorough understanding of polymer surface interactions will result in major advances in processing, not just in problems of extrusion instability but, more importantly, in our ability to tailor surfaces for specific processing functions. I remain convinced that many of the extrusion instabilities which we have been studying (for I do not believe there is just one, despite the common onset at about the same recoverable shear) are the result of surface interactions, and that this is a fruitful avenue for research. It is likely that other mechanisms (stress-induced phase transitions, for example) are also important, and the recurrent danger is to become so focused on one idea that we miss other possibilities. We have done this too often in the past.

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REFERENCES


MICROHYDRODYNAMICS: PRINCIPLES AND SELECTED APPLICATIONS

by Sangtae Kim, Seppo J. Karilla
Butterworth-Heinemann, 80 Montvale Avenue, Stone, MA 02180; 507 pages, $69.95 (1991)

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There has been a long-standing need for a comprehensive book that discusses analytical, asymptotic, and numerical methods for computing the motion of particles in creeping flows and that catalogues known solutions, which can be used as a reference by instructors, students, and researchers. This book satisfies that need and does so in a well-organized, meticulous, proficient, and imaginative manner. The topics presented in the book, along with those in the classical monograph by Happel and Brenner (Low Reynolds Number Hydrodynamics) should be required reading for students of fluid mechanics, colloidal science, and other engineering disciplines involving particulate flows.

The main theme of the book concerns the question of how to compute the structure and properties of creeping flow past a single particle or a collection of particles of arbitrary shape in the presence of solid boundaries, and the alternative methods for this computation. The answer is given in the various chapters that are organized according to the geometrical conditions surrounding the problem. In the interest of rigor and comprehension, the mathematical developments are introduced with an illuminating discussion of the general properties of creeping flow, including variational principles.

One important and pioneering contribution this book makes is an instructive discussion of boundary integral representations in a manner that is coherent, rigorous, and accessible to readers with a fundamental background in functional analysis and integral equation theory. The application of methods of functional analysis and operator theory to study the properties of the integral equations of Stokes flow will be a

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