Experimental Evidence for an Intrinsic Route to Polymer Melt Fracture Phenomena: A Nonlinear Instability of Viscoelastic Poiseuille Flow

Volfango Bertola,[1] Bernard Meulenbroek,[2] Christian Wagner,[1] Cornelis Storm,[2] Alexander Morozov,[2] Wim van Saarloos,[1,2] and Daniel Bonn[1]

[1]*Ecole Normale Supérieure, Laboratoire de Physique Statistique, 24 Rue Lhomond, 75005 Paris, France*
[2]*Instituut-Lorentz, Universiteit Leiden, Postbus 9506, 2300 RA Leiden, The Netherlands*

(Received 13 February 2002; published 17 March 2003)

The production rate of polymer fibers by extrusion is usually limited by the appearance of a series of instabilities (''melt fracture'') that lead to unwanted undulations of the surface. We present both qualitative and quantitative experimental evidence that—in addition to previously known polymer-specific scenarios—there is an intrinsic route towards melt fracture type phenomena: a nonlinear (''subcritical'') instability of viscoelastic Poiseuille flow.

DOI: 10.1103/PhysRevLett.90.114502 PACS numbers: 47.20.Ft, 83.50.–v, 83.80.Sg

The study of flow instabilities goes back several centuries. Much progress has been made, especially over the last decades, and most ''simple'' instabilities are well understood by now. Less well understood are flow instabilities in complex fluids. The unusual non-Newtonian flow properties of complex fluids can not only modify existing instabilities such as viscous fingering [1] but they can also give rise to completely new instabilities and flow behavior [2–8]. In this Letter we present evidence that a viscoelastic flow instability that is absent for Newtonian fluids underlies an important set of phenomena that occur in the spinning of polymer fibers, and that have plagued the plastic industry ever since the first plastic fibers were produced. Our work gives strong evidence that when other effects that can give rise to irregular flow behavior for specific polymers or flow geometries are suppressed, an intrinsic viscoelastic instability will always remain.

The manufacturing of plastics is one of the most important industrial manufacturing processes, and is used to create a huge variety of objects. The most common process is extrusion, in which polymer fibers or sheets are produced by forcing the polymer melt or solution through a cylindrical hole or slit (a ''die'') [6]. The production speed in virtually all plastic extrusion processes is essentially always limited by the appearance of unwanted long wavelength undulations of the surface [5,6,9–11]. The generic name for these phenomena which develop when the extrusion velocity is higher than some critical value is called melt fracture, in reference to the fact that the extrudate can even break for the highest speeds. It is clear that there is no unique route to melt fracture and that the detailed behavior depends on the polymer that one uses, the shape of the ''die,'' etc. There is, for instance, ample evidence that the short wavelength distortions which are usually referred to as ''sharkskin'' are due to a quasiperiodic adhesion of the material near the outlet. Likewise, the spurt-flow regime is usually attributed to stick-slip behavior of the polymer inside the die. We will present experimental evidence that besides these routes to irregular behavior which depend on the specific polymer or die shape, there is at least one fundamental *intrinsic* route to melt fracture which is common to all polymeric fluids which exhibit so-called normal stress effects. The scenario which we advance here experimentally, and theoretically in a companion paper [12], is that while viscoelastic Poiseuille flow in the die is linearly stable to perturbations of infinitesimal amplitude, so-called normal stress effects drive it nonlinearly unstable to perturbations of small but finite amplitude. Such an instability is called a weakly subcritical bifurcation.

It has long been known that Poiseuille flow of a so-called Oldroyd-B or UCM model [13,14] (among the simplest polymer models that exhibit normal stress effects) is linearly stable [15]. Nevertheless, tabulated values for a whole range of different polymers indicate that a bulk flow instability occurs when elastic stresses become comparable to viscous stresses [11]. As we discuss in [12], this observation together with the guidance provided by the subcritical instability observed in viscoelastic Taylor-Couette flow [2–4,7] and the subcritical transition to turbulence for ordinary fluids leads one to suspect the existence of an underlying nonlinear viscoelastic flow instability. The results from a weakly nonlinear amplitude expansion presented in [12] do indeed confirm this suggestion explicitly. In this Letter we present qualitative as well as quantitative experimental evidence for this scenario: (i) for our experimental model system other common instability mechanisms such as those described above are not present but nevertheless the onset of irregular flow behavior occurs at values comparable to those listed in the engineering literature for a whole range of polymer solutions and melts [11]; (ii) the difference in threshold value in between a cylindrical and slit die is in good agreement with the theoretical calculations; (iii) we observe a hysteresis that one expects near such a ''first-order-like'' subcritical transition; (iv) without adjustable parameters our experimental results compare well with our theoretical predictions [12] for the frequency of the

surface distortions and with recent numerical simulations published after submission of this paper [16].

We study extrusion experimentally for a polymer/crosslinker system (polyvinyl alcohol/sodium tetraborate) for which changing the crosslinker concentration allows variation of the viscoelastic properties of the system: the relative importance of the viscous and elastic stresses can be changed in a continuous fashion [17]. The aqueous polymer solution contained in a cylindrical reservoir is forced to flow through a cylindrical glass die by a piston driven by a step motor. We first discuss our visual observations, and then discuss the characterization of our solutions and our quantitative measurements.

For low extrusion velocities the flow is perfectly smooth, until a critical flow rate is reached for which slight irregularities can be noticed on the extrudate surface; subsequently the surface becomes very rough, as Fig. 1 illustrates. Measurement of the diameter of the extrudate from a direct visualization using a CCD camera shows that the appearance of significant roughness occurs at a well-defined extrusion speed (Fig. 2), corresponding to a well-defined (average) shear rate in the die. The more surprising observation is that the surface distortions appear at higher shear rate upon increasing the extrusion velocity than the shear rate at which they disappear upon decreasing the speed — see Fig. 2. In other words, the transition from a smooth to a corrugated surface is found to exhibit a dynamical hysteresis, and the extent of the hysteresis interval depends on the time the system is given to reach a dynamical equilibrium state. This is a clear signal of the subcritical nature of the transition, very much like the hysteresis in a thermodynamic system is normally a strong sign of a first-order transition. It should be noted that the observed hysteresis is not due to a slow viscoelastic relaxation of the polymer solutions: their longest relaxation time is of the order of a second, whereas for each measurement of Fig. 2 the extrusion speed is altered only after 30 sec. In addition, the residence time in the die can be estimated for the shortest die as $4R/(D^*\dot{\gamma}) \approx 8$ s at the onset of instability (see Table I). That the observed hysteresis is unlikely to be caused by an instability at the die entrance is indicated by the observation that the hysteresis does not depend significantly on the length of the capillary.

To quantify the bulk viscoelastic properties of our solutions, we determined the viscous stress σ_v and the first normal stress difference N_1 for the different solutions as a function of the shear rate $\dot{\gamma}$ in the relevant shear rate range using a Reologica Stress-Tech stress-controlled cone-plate rheometer with a 40 mm/4° cone. The first normal stress difference is the first-order elastic effect for polymer solutions and melts. It is usually interpreted as being due to the stretching and/or orientation of the polymer chains by the flow. The entropic tendency of polymers that are stretched by the flow to recover their equilibrium chain conformation generates an elastic stress, the macroscopic manifestation of which is a difference in stress between the flow direction and the direction normal to it [13,14], called the first normal stress difference N_1. Our rheology measurements illustrated in Fig. 3 show that for not too high shear rates the viscosity η of our solutions is almost constant: the viscous stresses are consequently given by $\sigma_v = \eta\dot{\gamma}$. The first normal stress difference N_1 increases quadratically with the shear rate: $N_1 = \Psi_1\dot{\gamma}^2$, Ψ_1 being the first normal stress coefficient. This naturally defines [13,14] the viscoelastic relaxation time of the solution as $\tau = (\Psi_1/\eta)$. Moreover, the ratio of the elastic to the viscous stresses at the wall, the Weissenberg number $\mathrm{Wi} = N_1/\sigma_v = \dot{\gamma}\tau$, is then a linearly increasing function of the shear rate: The flow is predominantly viscous

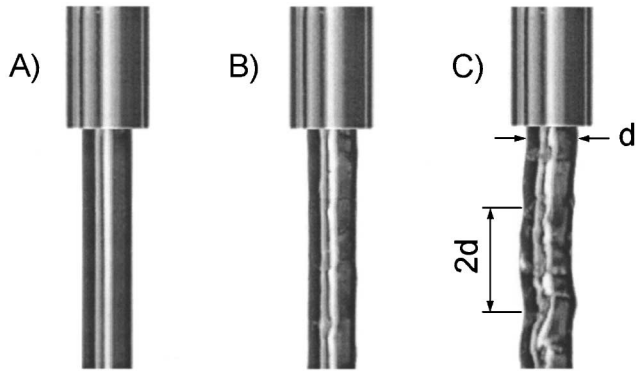

FIG. 1. Direct observation of the extrusion for different speeds for a 0.4% borax solution: (a) for the lowest speed (Wi = 2.8) the surface is smooth (b) intermediate speed (Wi = 4.9): development of a small roughness (c) at the highest speed (Wi = 8.4) the melt fracture is well developed.

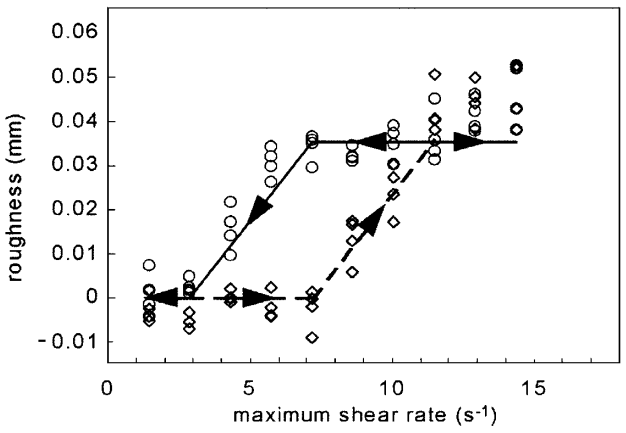

FIG. 2. The root mean square amplitude of the extrudate surface roughness (obtained by analyzing the pictures) as a function of the maximum shear rate inside the capillary. For low shear rates the roughness is almost constant (smaller than one pixel), while for shear rates greater than a critical value it becomes much larger, so the transition to melt fracture is well defined. Note the dynamical hysteresis obtained upon increasing (diamonds) and decreasing (circles) the extrusion speed.

TABLE I. Values for the onset of instability for different concentrations and different geometries used in the experiment. We changed the aspect ratio L/R of the die; the aspect ratio of 54 is for a radius of 0.75 mm, the others are for a radius of 1.25 mm. We also changed the form of the inlet from flat to conical; the opening angle of the cone is 90°.

L/R	Inlet	Borax (%)	$\tau = \Psi_1/\eta$ (s)	Wi
16	flat	0.2	0.362	5.61
54	flat	0.3	0.354	5.69
16	flat	0.3	0.354	4.81
16	flat	0.4	0.414	5.03
54	flat	0.5	0.386	4.24
16	flat	0.5	0.386	4.05
16	flat	0.5	0.386	3.98
16	cone	0.5	0.386	4.11
32	flat	0.5	0.386	3.91
32	cone	0.5	0.386	3.98
64	flat	0.5	0.386	3.85
64	cone	0.5	0.386	5.77
Slit	flat	0.2	0.362	14.15
Slit	flat	0.3	0.354	12.51
Slit	flat	0.4	0.414	10.73
Slit	flat	0.5	0.386	9.21

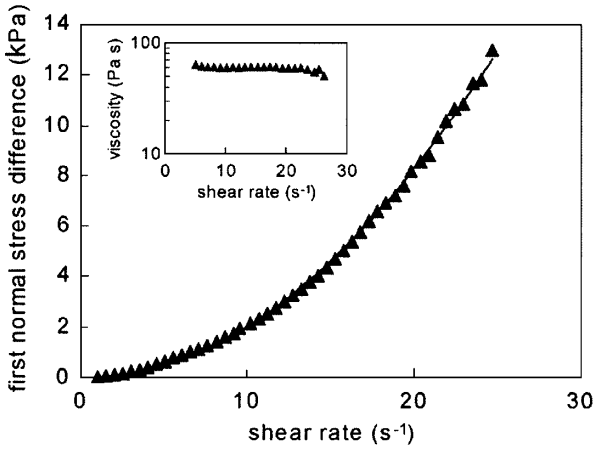

FIG. 3. Elastic (normal) stresses and viscosity (inset) as a function of the shear rate measured on a Reologica Stress-Tech rheometer with a 40 mm/4° cone-plate geometry for a 0.2% borax solution. The line is a fit to a quadratic shear-rate dependence, corresponding to the Oldroyd-B model. For higher shear rates and depending on the crosslinker concentration, the solution becomes strongly shear thinning, which is the usual observation for polymer solutions and melts exhibiting melt fracture. However, it has already been established (Ref. [8]) that the first instabilities, which interest us here, occur before this shear thinning region; these two phenomena appear to be disconnected.

for low extrusion speeds, but becomes dominated by elastic stresses at high speeds. The fact that over the range where we perform our measurements η and Ψ_1 are essentially constant makes it legitimate to compare our data quantitatively with the predictions [12] for the UCM, as this is precisely the constitutive equation that captures this behavior. In the UCM or Oldroyd-B model, the laminar Poiseuille flow profile is parabolic [13]. Hence, from the flow rate through the cylinder at which the instability occurs and the fact that it is legitimate to assume the laminar flow to be parabolic up to the transition, we can calculate the shear rate at the wall and hence the critical Weissenberg number Wi. We have also checked that in our experiments the die swell at the outlet is of the same order as calculated in [18], although in the experiments shown in Fig. 1 where the viscosity is not too high, it is attenuated by the effects of gravity, which are not taken into account in [18].

Our experimental values for the critical Weissenberg number are tabulated in Table I. We find that the onset of the surface roughness occurs at $\mathrm{Wi} = 4.6 \pm 0.6$ which is precisely the same range reported in [11] for 20 technologically important polymer solutions and melts with viscosities varying over 3 orders of magnitude. However, those systems show shear thinning, so that a direct comparison with the UCM model is not feasible. For our polymer solutions, whose rheology closely follows the model predictions, within our experimental accuracy the critical Weissenberg number is independent of the crosslinker concentration (and hence viscosity) and of the aspect ratio of the die. In addition, we have changed the form of the inlet from flat to conical. This changes the secondary flows near the die entry; however, the critical Weissenberg number is still around 5.

Our experimental value for the critical Weissenberg number compares well with the results for the weakly nonlinear expansion [12]. Although it is impossible to identify a unique threshold for a subcritical bifurcation, these calculations for the UCM model indicate that normal stress effects can give rise to quasiperiodically modulated flow in the cylindrical die for Weissenberg numbers above 5; for Weissenberg numbers of order 8, perturbations as small as 4% were found to be sufficient to drive the laminar flow profile unstable [12]. Whether or not the spread in our experimentally determined critical value is related to the fact that for a subcritical bifurcation the effective threshold value may depend on the experimental protocol, we do not know at present.

Further evidence for the consistency of our experimental and theoretical results comes from a series of experiments using a slit die (as for making polymer sheets). As the results listed in Table I show, the critical Weissenberg number for the slit is about a factor of 3 larger than for the cylindrical die. This is consistent with the theoretical finding [12] that the threshold amplitude for the slit is at least a factor of 2 larger than for the cylindrical die.

We finally address the frequency spectrum of the diameter thickness variations. If these are indeed the remnants of the predicted finite wavelength modulation of the flow profile in the capillary, the frequency of the

perturbations outside the die can be predicted from the critical wave numbers assuming that the instability is advected at the mean flow velocity. From the results for the band of wave numbers where the subcritical instability is found, one then finds for the frequency f of the modulations $0.3v/R < f < 0.72v/R$ where v is the mean velocity and R the die radius in the experiments [12]. In Fig. 4 we plot the value of the main frequency of our time series of the diameter thickness for various Weissenberg numbers; the two lines indicate the boundaries of the range of allowed frequencies according to [12]. Clearly, our experimental data fall nicely in the predicted frequency range. Note that this comparison is made without any adjustable parameters.

Melt fracture was observed for the first time during the 1950s [5,6,9,10], when the use of plastic materials instead of metals became widespread. In this Letter we have presented experimental evidence that for our system, for which stick-slip and outlet instabilities are absent, the appearance of considerable surface roughness of the extrudate can be understood as an elastically driven, subcritical bulk instability of the flow in the die. As the ratio of the viscous to the normal stresses is the only parameter of the problem, and as it can be influenced [19] by the polymer chemistry (for instance the degree of branching) or by additives, it might be feasible to control the appearance of gross melt fracture in practice. As very similar instabilities have been reported for injection molding of plastics [6], the standard way of making hollow plastic objects, our results may also apply to this problem. On a more fundamental level, we have shown here that normal stress effects can render Poiseuille flow of complex fluids unstable. Although elastically driven instabilities in geometries with curved streamlines (e.g., Couette flow [2–4,7]) are well accepted, normal pipe flow was believed to be stable because of the fact that the streamlines are not curved. However, this argument only implies that the flow is linearly stable: once perturbation is present, the streamlines are curved and thus the "perturbation of the perturbation" renders the flow unstable — in other words the flow is linearly stable but nonlinearly unstable.

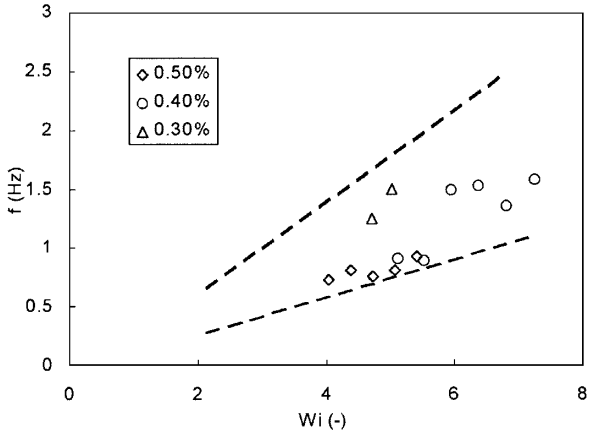

FIG. 4. Characteristic frequency of the instability for different borax concentrations, determined from the location of the peak in power spectra of diameter thickness fluctuations time series. The dashed lines delimit the frequency associated with the unstable band calculated in the nonlinear stability analysis.

Finally, the subcritical nature of the instability allows one also to understand the dependence of the onset of melt fracture on the die material reported in the literature. In fact, different materials will have a different wall roughness, which in turn can lead to slightly different fluctuations in the flow velocity during extrusion. As the perturbation needs to have a finite amplitude to grow in case of a subcritical bifurcation, this can lead to a retarded appearance of melt fracture for smooth die walls. The same might hold for the shape of the inlet and the outlet. However, the origin of the bifurcation is still the same, and is still driven by the bulk viscoelastic properties of the polymer if other instabilities do not preempt this intrinsic flow instability.

We thank Jacques Meunier for helpful discussions. LPS de I'ENS is UMR 8550 of the CNRS associated with the universities Paris six and Paris 7.

[1] D. Bonn and J. Meunier, Phys. Rev. Lett. **79**, 2662 (1997).
[2] R. G. Larson, E. S. G. Shaqfeh, and S. J. Muller, J. Fluid Mech. **218**, 573 (1990).
[3] R. G. Larson, Rheol. Acta **31**, 213 (1992).
[4] E. S. G. Shaqfeh, Annu. Rev. Fluid Mech. **28**, 129 (1996).
[5] M. M. Denn, Annu. Rev. Fluid Mech. **22**, 13 (1990).
[6] M. M. Denn, Annu. Rev. Fluid Mech. **33**, 265 (2001).
[7] A. Groisman and V. Steinberg, Phys. Fluids **10**, 2451 (1998); Nature (London) **405**, 53 (2000).
[8] R. G. Larson, Nature (London) **405**, 27 (2000).
[9] J. P. Tordella, J. Appl. Phys. **27**, 454 (1956).
[10] J. P. Tordella, in *Rheology: Theory and Applications*, edited by F. R. Eirich (Academic Press, New York, 1969), Vol. 5, pp. 57–92.
[11] M. Pahl, W. Gleissle, and H. M. Laun, *Praktische Rheologie der Kunststoffe und Elastomere* (VDI Verlag, Hamburg, 1991).
[12] B. Meulenbroek, C. Storm, V. Bertola, C. Wagner, D. Bonn, and W. van Saarloos, Phys. Rev. Lett. **90**, 024502 (2003).
[13] R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (Wiley, New York, 1987).
[14] R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, Oxford, 1999).
[15] C. Ho and M. M. Denn, J. Non-Newtonian Fluid Mech. **3**, 179 (1978).
[16] K. Atalik and R. Keunings, J. Non-Newtonian Fluid Mech. **102**, 299 (2002).
[17] A. Takada, M. Nishimura, A. Koike, and N. Nemoto, Macromolecules **31**, 436 (1998).
[18] R. I. Tanner, J. Polym. Sci. **A2**, 2067 (1970).
[19] F. W. Billmeyer, *Textbook of Polymer Science* (Wiley, New York, 1984).