

Separation of Elastic and Viscous Effects in Polymer Melt Extrusion

H. P. SCHREIBER, A. RUDIN, and E. B. BAGLEY, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

Synopsis

Viscosity and elasticity of polymer melts respond differently to changes in extrusion conditions and to thermal and shear history of the polymer sample. Some reasons for this difference in behavior are summarized in this communication, which also presents new data on the topic. The results are rationalized on the basis of chain flexibility and interaction concepts, permitting the prediction of certain experimentally verifiable aspects of polymer melt rheology.

Viscous and elastic effects in polymer flow have been separated by Bagley,¹ who applied concepts due to Philippoff and Gaskins² to show that the end correction in the capillary extrusion of polyethylene could be divided into a viscous component (Couette correction) and an elastic component (recoverable shear). This work indicated that the true melt viscosity of polyethylenes was independent of orifice length. In a subsequent paper³ on post-extrusion swelling in polyethylenes it was found that melt elasticity varied with the total shear strain and thus depended on orifice length, at constant shear stress. As before, however, true viscosity was independent of die length. Similarly, Tordella⁴ concluded from birefringence data that the elastic strain in polymer flow varied down the capillary although the viscosity change was very small. Elastic parameters in general, therefore, seem to depend on orifice length in capillary extrusion, while polymer viscosity does not.

Flow studies of certain linear polyethylene fractions further distinguish between viscous and elastic effects.⁵ In contrast with whole polymers of the same weight-average molecular weight these fractions were found to have essentially zero end corrections. In addition, the degree of post-extrusion swelling and the rate of change of swelling with extrusion pressure were very much lower than in whole polymers. The swelling effects also appeared to be time-dependent, increasing with the residence time of fractions in the viscometer at a temperature well above the melting point. Since the absence of elastic effects was noted for sharp fractions as well as blended fractions,⁵ factors other than molecular weight distribution are responsible. It was proposed that a long-range, elastically deformable entanglement network responsible for elastic effects in flow was diminished by

the solution treatment involved in polymer fractionation and was only partially re-established in the experimental time. It is important to know whether the viscosity of such polyethylene fractions is also affected by the solution treatment during fractionation. Relevant experiments and discussion are presented in this paper.

Experimental

The fractionated linear polyethylene used in this work was fraction F-2 of a previous study⁵ which has a \overline{M}_w value of 105,000 and an apparent distribution width ($\overline{M}_w/\overline{M}_n$) of 1.9. Extrusion experiments were carried out by use of the familiar C-I-L high shear viscometer fitted with a flat-entry capillary die with $L/R = 7.64$ and radius = 0.104 cm. The pertinent experimental results are listed in Table I.

Viscosity and elasticity parameters were measured for the polyethylene fraction after various relaxation periods in the capillary viscometer at 190°C. and the results compared with the first control extrusion, which involved a standard 15-min. preheat period. Clearly, there is a marked recovery in elastic properties of the sample, while the apparent viscosity remains essentially unchanged. The viscosity of this sample, and of others showing abnormally low extrudate swelling effects, agree with previously reported results.⁵ The data in Table I show that the recovery of elastic properties cannot be attributed to thermal instability of the material, which would have caused a concurrent change in viscosity. To avoid the danger of thermal instability, relaxation periods were limited to 2 hr., but it seems unlikely that the fractionated polymer would attain the high B and B_p values of the whole polymer if a steady state had been reached. The probable difference in steady-state elasticity parameters suggests some dependence of melt elasticity on molecular weight distribution.

TABLE I
Comparison of Viscous and Elastic Effects after
Various Relaxation Periods^a

Sample history	Viscosity parameters ^b		Elasticity parameters ^c	
	$\eta_0 \times 10^{-5}$	$\eta_{200} \times 10^{-4}$	B_{100}	B_p
Control extrusion	2.44	3.85	1.22	0.13
0.5 hr. at 190°C.	2.51	3.70	1.29	0.19
1.0 hr. at 190°C.	2.47	3.77	1.36	0.23
2.0 hr. at 190°C.	2.41	3.69	1.41	0.26
Whole PE with $M_w = 10^6$	2.60	—	1.60	0.88
η_0 expected from $\eta_0 - M_w$ function for PE	2.51	—	—	—

^a Linear polyethylene fraction F-2⁵ $M_w = 1.05 \times 10^6$; extrusion at 190°C.; flat entry die $L/R = 7.64$; $R = 0.104$ cm.

^b η_0 = apparent Newtonian melt viscosity, determined as described by Schreiber et al.;⁶ η_{200} = apparent melt viscosity at 200 psi extrusion pressure.

^c B_{100} = extrudate to die diameter ratio at 100 psi extrusion pressure; B_p = slope of linear B vs. $\log P$ plot.⁵

A pronounced effect of prior solution treatment on polymer elasticity was also noted in the work of Philippoff,⁷ who observed strong reductions in the birefringence of polystyrene solutions after filtration, while surprisingly, solution viscosity remained unchanged. These results can also be interpreted as showing the break-up of an entanglement network, in this case by the filtration process.

Discussion

The experimental results summarized above show that in the cases studied, die transit or solution treatment of a polymer changes the degree of chain interaction sufficiently to affect polymer elasticity, but not sufficiently to also influence polymer viscosity. These results are anomalous in terms of the segmental entanglement theory of Bueche,⁸ since that theory in effect attributes both viscous and elastic behavior in polymers to segmental entanglements. This concept is oversimplified, viscosity and elasticity in polymer flow apparently arising from entanglement interactions of different character. A possible means of resolving the anomaly is suggested below.

First consider polymer viscosity. For any essentially linear polymer a critical molecular weight, M_c , exists at which the slope of the $\log \eta_0$ versus $\log M$ plot changes abruptly from about 1.0 to a value near 3.5. η_0 is the zero shear viscosity in this case and M is, generally, the weight-average molecular weight of the polymer. The abrupt increase, above M_c , in the rate of change of melt viscosity with molecular weight may be attributed to a sudden increase in the degree of coordination in segmental motion necessary for random motion of the polymer molecule as a whole. Segmental entanglements are usually taken to be responsible,^{8,9} M_c being the minimum molecular weight for sufficient chain flexibility to permit either intramolecular or intermolecular segmental couplings.

In the cited experiments polymer viscosity does not change to any detectable extent during the passage through the die orifice. Evidently, the coordination requirement for the movement of an average chain segment and the number of segments whose coordination is needed for molecular motion during passage through the die remains essentially unchanged from the state existing in the die entry region. Furthermore, at given shear stress these segmental coordination requirements must be established very rapidly, regardless of the effect of polymer sample history.

Some changes in the entanglement-disentanglement state must be occurring, however, to account for the changing value of elasticity parameters during die transit, or following solution treatment. This focuses attention on the origin of melt elasticity. Some proportion of the observed melt elasticity doubtless arises from deformation of the molecules due to compression, and this will be substantially unaffected by chain entanglements. The remainder, which largely accounts for the effects described above, probably arises from the deformation of an elastic network, established by long-range chain entanglements.

Such an elastic network can be established by the segmental entanglement mechanism provided the polymer chains are sufficiently long and flexible to crosslink effectively, even if only temporarily. A particular chain can contribute to the network, however, only when it interacts in this manner with at least two different chains. This concept therefore calls for a critical molecular weight, $(M_c)_e$, for the onset of melt elasticity. If the entanglement frequency is defined by M_c , then a lower limit for $(M_c)_e$ is given by $(M_c)_e = 2M_c$ (cf. Bueche⁸ and Schreiber¹⁰). Because of the restriction that only chains cross-linking with two different molecules can contribute to elasticity, however, it is expected that, in general, $(M_c)_e$ will be considerably greater than $2M_c$. This contention appears to be supported by the calculations of Gill and Toggenburger.¹¹ Using birefringence data for solutions of polystyrenes having molecular weights in the vicinity of 10^6 , these authors calculate an entanglement frequency of about 3 per molecule. M_c in this case being about 40,000, this suggests that $(M_c)_e \simeq 8M_c$ for polystyrene.

In most thermoplastics the segmental size is likely to be considerably less¹² than M_c . Apparently, therefore, in a polymer sample showing viscoelasticity the number of interacting segments (which determine melt viscosity) is much greater than the number of effectively crosslinked chains (which determines melt elasticity). Any change in interchain entanglements resulting from die transit or solution treatment therefore produces proportionally much greater changes in the number of effectively crosslinked chains constituting the elastic network than in the number of interacting segments cooperating during molecular translation. This concept would appear to be reasonable provided the distance between network crosslinks is much larger than the segmental length. When chain entanglement spacing and segmental size are of the same order of magnitude, however, or when the number of segments per polymer chain becomes small, then a shift in the state of entanglement of the polymer during die transit could conceivably influence the mobility of individual chain segments. Thus a response in viscosity to changing orifice length and to solution treatment is more likely to be observed under appropriate conditions with a stiffer molecule (like polystyrene) than with relatively flexible chains (like those of polyethylene or polyformaldehyde) and at low molecular weights of a polymer in the neighborhood of M_c .

We may also note here that the influence of molecular weight on network elasticity can be described by expressions of the type¹³

$$\mu = RT\rho/M \quad (1)$$

where μ is the elastic modulus, R and T have their usual meaning, ρ is the melt density, and M is the molecular weight between crosslinks. Logically, M should be a number-average molecular weight. Actually, for polyethylene,¹ application of this expression to results of capillary extrusion ex-

periments has led to calculations of M values of the same order of magnitude as the weight-average molecular weight of the bulk polymers. This result may be due to the fact that very large molecules in a polydisperse system contribute disproportionately both to the establishment of the elastic network and to the light scattering which determines the experimental M_w value. In that case the molecular weight between crosslinks will be a number-average for the high molecular weight species present. This molecular weight will of course correspond more closely to the M_w than to the M_n of the whole sample.

Consequences

A number of experimentally verifiable consequences result from the foregoing discussion.

(1) Steady states in long-range entanglements are apparently attained slowly in thermoplastic melts under the usual conditions. Melt elasticity parameters therefore depend significantly on the history of the sample, solution treatment and previous shear and high temperature exposure, etc. being important in this context. For any fixed set of capillary extrusion conditions, the measured elasticity values may not necessarily be representative of the thermodynamic equilibrium state of the melt. The importance of history effects should increase with the molecular weight, and melt viscosity, of the polymer. On the other hand, the true inelastic viscosity parameter of a polymer¹ should be independent of such history effects in those experiments involving polymers with segmental lengths which are much smaller than the average distance between chain entanglements.

(2) Since a minimum molecular weight, M_c , is necessary for segmental entanglements to influence bulk viscosity appreciably, a higher minimum molecular weight $(M_c)_e$ (probably $> 2M_c$), is expected for such interactions to produce an effective elastic network. Experimentally, $(M_c)_e$ should be defined by plotting an elastic parameter, such as recoverable shear or extrudate swelling, versus molecular weight, in analogy with the well-known η_0 versus M plot used to define M_c .^{6,9} Elasticity data would of course have to relate to equilibrium states of the melt. Monodisperse polymers with M intermediate between M_c and $(M_c)_e$ should display no network elasticity but should have non-Newtonian viscosities and should lie on the steeper leg (slope about 3.5) of the $\log \eta_0$ versus $\log M$ plot.

(3) At sufficiently low molecular weights, where the number of chain segments is small, (most probably in the vicinity of M_c for a given polymer) the independence of melt viscosity and die length in capillary extrusion should break down. Bagley's plot¹ of extrusion pressure versus die length over radius should therefore become nonlinear and may be expected to show an increase in viscosity with increasing die transit time.

References

1. Bagley, E. B., *Trans. Soc. Rheol.*, **5**, 355 (1961).
2. Philippoff, W., and F. H. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
3. Bagley, E. B., S. H. Storey, and D. C. West, *J. Appl. Polymer Sci.*, **7**, 1661 (1963).
4. Tordella, J. P., *J. Appl. Polymer Sci.*, **7**, 215 (1963).
5. Schreiber, H. P., and E. B. Bagley, *J. Polymer Sci.*, **B1**, 365 (1963).
6. Schreiber, H. P., E. B. Bagley, and D. C. West, *Polymer*, **4**, 355 (1963).
7. Philippoff, W., *Trans. Soc. Rheol.*, **7**, 45 (1963).
8. Bueche, F., *J. Chem. Phys.*, **20**, 1959 (1952).
9. Porter, R. S., and J. F. Johnson, *Trans. Soc. Rheol.*, **6**, 107 (1962).
10. Schreiber, H. P., *Polymer*, **4**, 365 (1963).
11. Gill, S. J., and R. Toggenburger, *J. Polymer Sci.*, **60**, S69 (1962).
12. Porter, R. S., and J. F. Johnson, *J. Appl. Polymer Sci.*, **3**, 200 (1960).
13. Wall, F. T., *J. Chem. Phys.*, **10**, 485 (1942).

Résumé

La viscosité et l'élasticité des polymères fondus répondent différemment aux changements des conditions dans lesquelles s'effectue l'extrusion ainsi qu'au traitement et au cisaillement de l'échantillon de polymère. Dans cette communication, on donne certaines raisons pour expliquer cette différence de comportement, et on présente également des données nouvelles sur le sujet. Les résultats sont rationalisés sur la base de concepts de flexibilité de la chaîne et d'interaction, ce qui permet de prévoir certains aspects expérimentaux vérifiables concernant la rhéologie des polymères à l'état fondu.

Zusammenfassung

Viskosität und Elastizität von Polymereschmelzen verhalten sich bei Änderung der Extrusionsbedingungen und bei verschiedener thermischer und Scherungsvorgeschichte der Polymerprobe verschiedenartig. In der vorliegenden Mitteilung werden einige Gründe für diese Unterschiede im Verhalten und auch darauf bezügliche neue Daten angegeben. Die Ergebnisse werden auf Grundlage des Kettenflexibilitäts- und Wechselwirkungskonzepts rationalisiert, was die Voraussage gewisser experimentell verifizierbarer Aspekte der Rheologie polymerer Schmelzen erlaubt.

Received March 30, 1964