

Post Extrusion Swelling of Polyethylene

E. B. BAGLEY, S. H. STOREY, and D. C. WEST, *Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec, Canada*

Introduction

In the extrusion of molten polymers from a reservoir through a capillary of length L and radius R it is found experimentally that P , the pressure, is linearly related to L/R at a constant shear rate.^{1,2} The relationship can be given by³

$$P = 2\tau_{tw}(L/R) + 2\tau_{tw}e \quad (1)$$

where τ_{tw} is the true shear stress at the capillary wall and e is an end correction term. The experimental results certainly indicate that τ_{tw} is independent of (L/R) at constant shear rate and hence the viscosity is also constant, independent of (L/R) . On this interpretation little of interest would appear to be occurring in the capillary. However, there are reports in the literature which indicate that some processes of considerable interest are taking place there. Clegg,⁴ referring to the results of Oakes and Peover, remarks that postextrusion swelling of polyethylene, at constant shear rate, is dependent on the capillary length-to-radius ratio. Similar results have been reported by others including Arai¹ and Burgess and Lewis,⁵ for polyethylene, and Kast⁶ for cuprammonium hydroxide solutions. The object of this work was to investigate this reported variation of extrudate swelling with capillary length.

Theory

It is generally observed that when liquids are forced from a reservoir through a capillary the extrudate diameter is not equal to the capillary diameter. Because Barus pointed this out, as a result of his studies on rubber systems (where the extrudate diameter is greater than the die diameter), the general effect is usually termed the Barus effect. Three basic qualitative explanations are commonly provided.^{1,4}

First, swelling arises as the approximately parabolic velocity distribution in the die transforms to a constant velocity distribution subsequent to extrusion, as discussed recently by Middleman and Gavis.⁷⁻⁹ Swelling from this effect should not be a function of the die length-to-radius ratio and hence will not be considered further here.

Second, swelling may be due partly to randomization of polymer molecules oriented during transit into the die.^{1,4,10} The simple analysis by

Spencer and Dillon¹⁰ seemed to lead to reasonable results but, as pointed out by Mooney,¹¹ the type of shearing deformation assumed by Spencer and Dillon should "only lead to a telescopic elastic deformation not to a longitudinal contraction and diametric swell." There are thus theoretical troubles here, but it is certainly conceivable that molecular randomization may well contribute to the swelling of the extrudate, particularly in the higher shear rate region. Again, as in the first case, the swelling should not vary with the capillary length-to-radius ratio if the molecular deformation and orientation are determined only by the shear stress and shear modulus, which appear to be independent of die length.¹²

For the purposes of this paper we shall assume, following Clegg⁴ and Arai,¹ that a third explanation of postextrusion swelling, termed the "memory effect," is needed to account for the variation of swelling with capillary length. This decay of swelling with capillary length might be expected to be a typical relaxation process, showing an exponential dependence on the time of transit through the die. If B , the swelling index, is defined as the ratio of extrudate diameter to die diameter and t is an average time of transit through the die, then an equation of the following form might be expected to hold:

$$(B - B_{\infty}) = (B_0 - B_{\infty}) \exp [-k t] \quad (2)$$

where B_0 and B_{∞} are values of B at zero and infinite transit times, respectively, and k is a decay rate constant. To rewrite eq. (2) in terms of L/R it is necessary to choose an average transit time. We have used a volume average transit or residence time, t_a , calculated as follows. If Q in cubic centimeters per second is the output rate through a capillary of radius R and length L , then

$$t_a = \pi R^2 L / Q \quad (3)$$

which may be written as

$$t_a = 4 (\pi R^3 / 4Q) (L/R) = 4 (L/R) / G \quad (4)$$

where G is the apparent Newtonian shear rate at the wall. A point arises here as to whether (L/R) , the actual capillary length-to-radius ratio, or $(L/R) + e$, the effective capillary length-to-radius ratio,¹² should be used. The latter value takes care of residence outside the capillary proper, and is the one considered here. Results for the actual capillary length case can be obtained easily by putting $e = 0$ in the appropriate expressions. Unless otherwise specified, results hold for both cases.

Equation (2) can now be written as:

$$(B - B_{\infty}) = (B_0 - B_{\infty}) \exp \{ -(4k/G) (L/R + e) \} \quad (5)$$

It will subsequently be necessary to have an expression for an average total shear strain for polymer which has passed through a capillary. The velocity profile in a capillary is given, for a Newtonian material, by

$$v = 2(R^2 - r^2)Q / \pi R^4 = (R^2 - r^2)G / 2R \quad (6)$$

The shear rate at a radial position, r , is, from eq. (6),

$$G_r = - (dv/dr) = (r/R)G \quad (7)$$

The time required for a particle to travel from the entry of the capillary to the point (r, l) is

$$t = 2lR/(R^2 - r^2)G \quad (8)$$

so the total shear, S_r , at the position (r, l) is

$$S_r = t G_r \quad (9)$$

$$= 2(l/r)/[(R^2/r^2) - 1] \quad (10)$$

To obtain an average shear the following procedure was used. Let \bar{v} be an average velocity so that

$$\bar{v} = Q/\pi R^2 \quad (11)$$

$$= (R/4)G \quad (12)$$

From eq. (6) it is seen that $v = \bar{v}$ at $r = R/\sqrt{2}$. The total shear at the same radial position will be used as the average shear, S . It is given by

$$S = 2\sqrt{2} [(L/R) + e] \quad (13)$$

where the effective capillary length $(L + eR)$ has been used for l . In general, $(L/R) + e$ will be considered proportional to the total average shear in a capillary.

Experimental

Experiments were carried out with a gas-driven capillary viscometer, previously described² (commercially available from Fischer and Porter (Canada) Ltd., Toronto, Ontario). End corrections were determined as usual² and, in addition, the diameter of the frozen extrudate, d , was measured. Actually, the diameter of the molten extrudate should be used to determine the value of B . This is difficult experimentally, so the value of B was computed from

$$B = (d/d_0) (\rho_s/\rho_m)^{1/2} \quad (14)$$

Where d_0 is the diameter of the capillary and ρ_s and ρ_m are the densities of the polymer solid and melt, respectively. The melt density figures used were those of Hunter and Oakes.¹³

The determination of B is not an accurate procedure. The solid densities are dependent on crystallization kinetics, as may be the extrudate shape. The swelling on emerging from the capillary may not be instantaneous and the extrudate tends to draw under its own weight. In this work efforts were made to standardize the actual measurement so that, while the absolute value of B may be in doubt, comparisons among capillaries of different (L/R) values are meaningful. The diameter of the extrudates

were all measured $1/4$ in. from the initially extruded end of the extrudate after the filament had been cut and cooled.

Results

Figures 1 and 2 illustrate the effects of die length on filament appearance for a polyethylene of low density and melt index¹⁴ 2 extruded at shear rates slightly above, and considerably above, the shear rate at which melt fracture¹⁵ occurs. In both cases it can be seen that the longer the capillary the smaller the extrudate diameter. Furthermore, the degree of distortion, which always accompanies melt fracture, is also strongly dependent on the die length-to-radius ratio; the shorter the die the worse the distortion. This variation of degree of distortion is also illustrated in Figure 3 for a low-density polyethylene of melt index 0.5. This latter polymer is a typical black compound—i.e., it contains 3 wt.-% carbon black—and shows not only the change of distortion with die length but also the change in gloss, the material extruded from the long die being considerably glossier than that extruded from a short die.

Quantitative measurements of the degree of extrudate swelling have been confined to shear rates below those at which melt fracture (and hence extrudate distortion) occurs. An example is given in Figure 4, where the swelling index B is plotted against L/R at two shear rates for a low-density melt-index-2 polymer. Since L/R is equivalent, at constant shear rate, to transit or residence time in the die, it is evident from the shape of the curves of Figure 4 why a relation of the type indicated in eq. (2) was chosen.

The same experiments which yielded the swelling data of Figure 4 also yielded the usual pressure and output data. When pressure at constant shear rate was plotted against L/R the usual straight-line relationships were obtained,^{1,2} indicating that the true shear stress and the viscosity were both constant and independent of L/R . Thus the very large change observed in extrudate swelling was not accompanied by any change in the measured viscosity. The two effects are thus either not related or else the degree of swelling "pressure" must affect the viscosity in such a minor way as to have no measureable effect. Basically, the same conclusion was arrived at by Tordella. In a very fine paper he showed that birefringence, and hence the elastic strain, can vary down the capillary but that the energy dissipation associated with the decreasing birefringence appeared to be small.¹⁶

Swelling decay data of the type shown in Figure 4 was fitted to eq. (5) (with a Bendix G-15-D computer) by a least-squares method. The results for various shear rates are given in Table I along with corresponding values of the end correction and the true shear stress at the wall.

From Table I it can be seen that B_{∞} and k are unchanged whether e is set equal to zero or not. The equilibrium swelling and rate constant do not depend on the chosen zero point. B_0 does change if $e = 0$ is used, although in neither case does the particular value of B_0 seem to reflect the apparatus dimensions. The B_0 value computed with the use of $(L/R) + e$ gives a

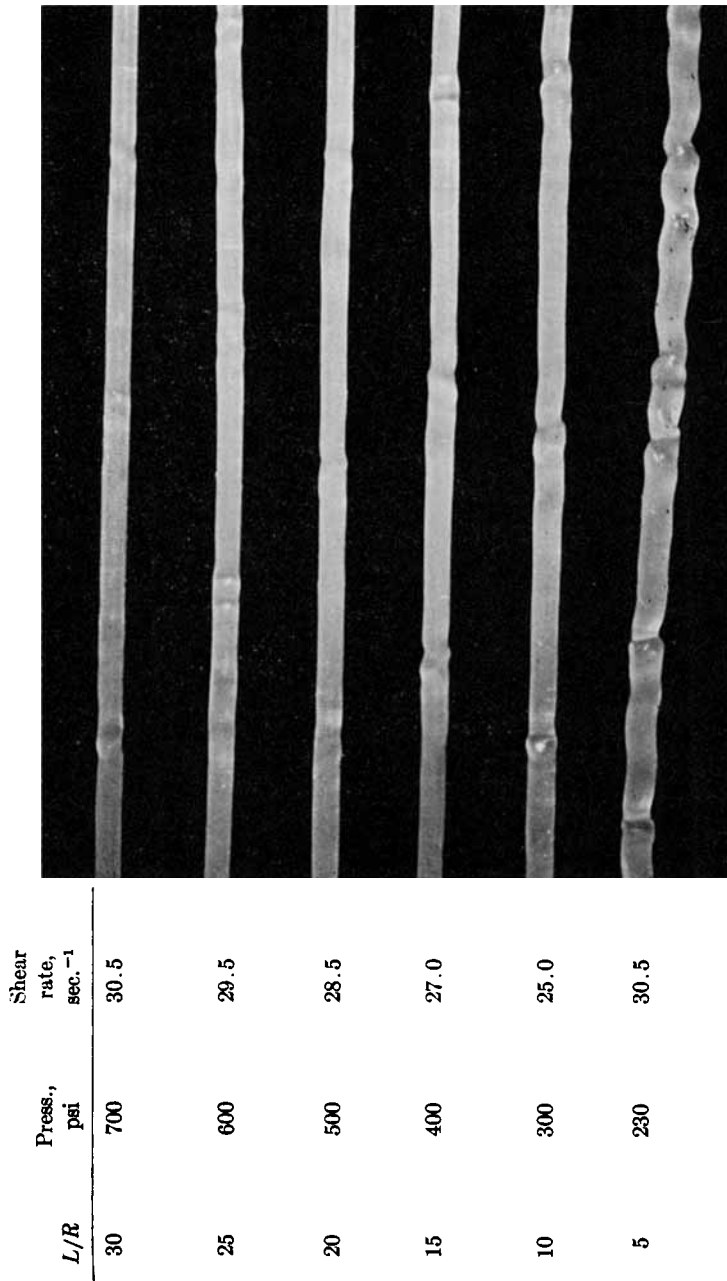


Fig. 1. The effect on extrudate appearance of changing the capillary length-to-radius ratio for a low-density melt-index-2 polyethylene at shear rates slightly above that at which melt fracture begins ($T = 190^{\circ}\text{C}$).

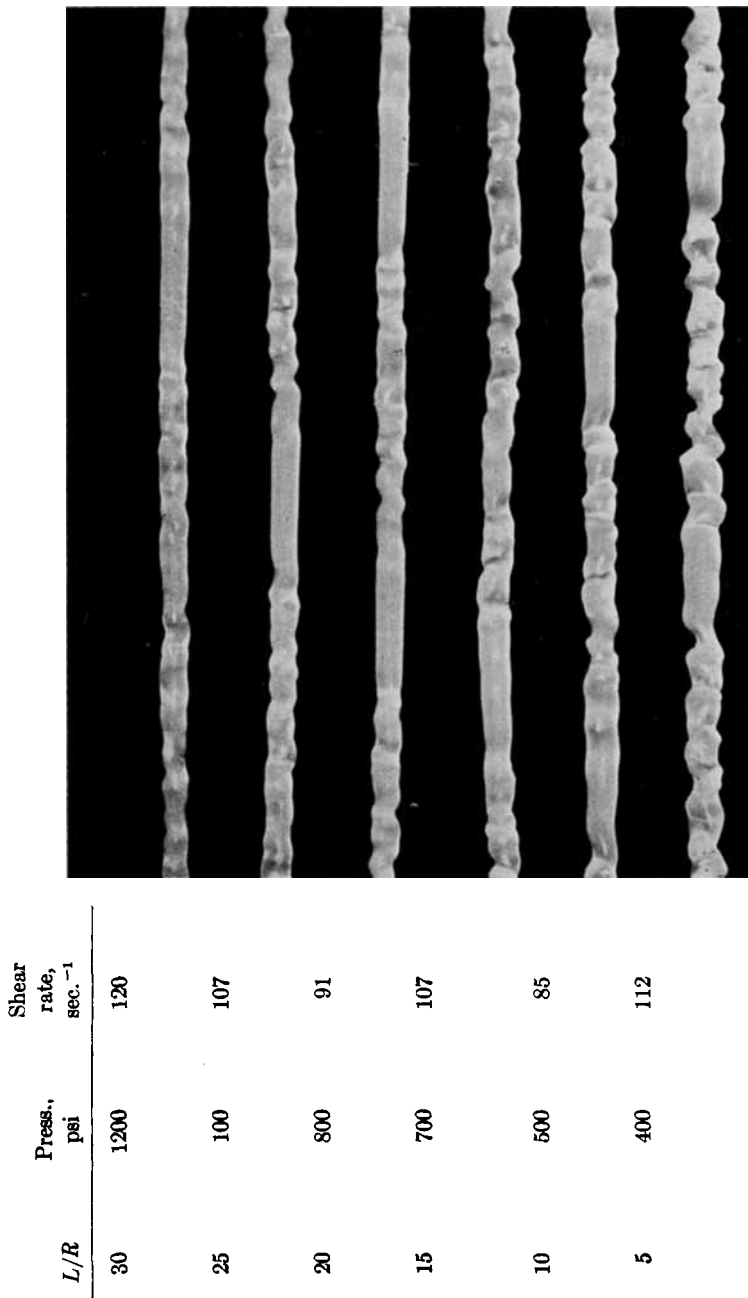
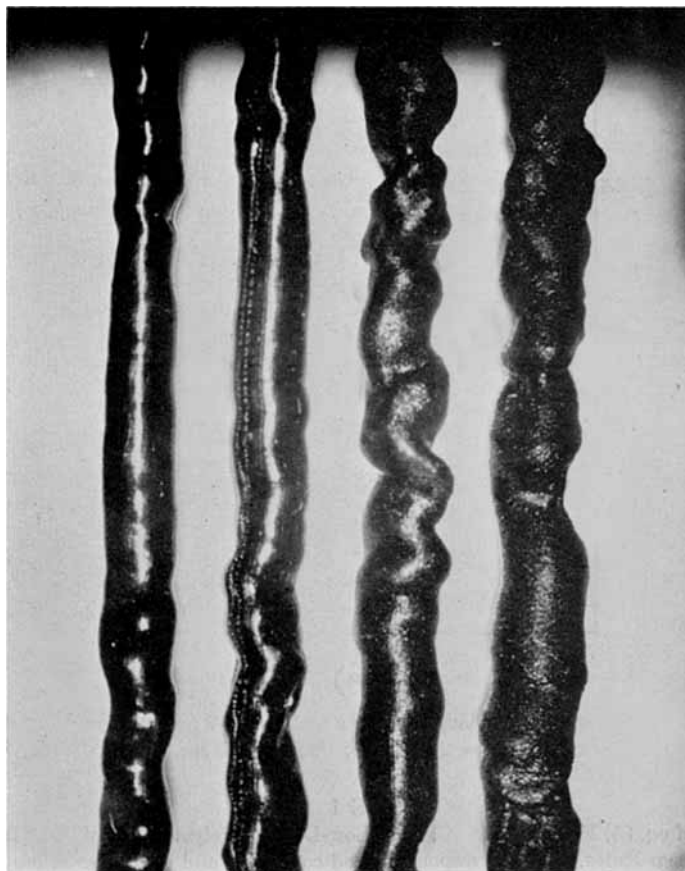


Fig. 2. The effect on extrudate appearance of changing the capillary length-to-radius ratio for the polyethylene shown in Figure 1. The shear rate is well above that at which melt fracture begins ($T = 190^{\circ}\text{C}.$).



L/R	Press., psi	Shear rate, sec. ⁻¹
29.9	1600	232
20.1	1200	265
9.96	800	289
4.94	550	260

Fig. 3. The effect of capillary length-to-radius ratio on both the degree of distortion and gloss for a melt-index-0.5 polyethylene ($T = 190^{\circ}\text{C}.$).

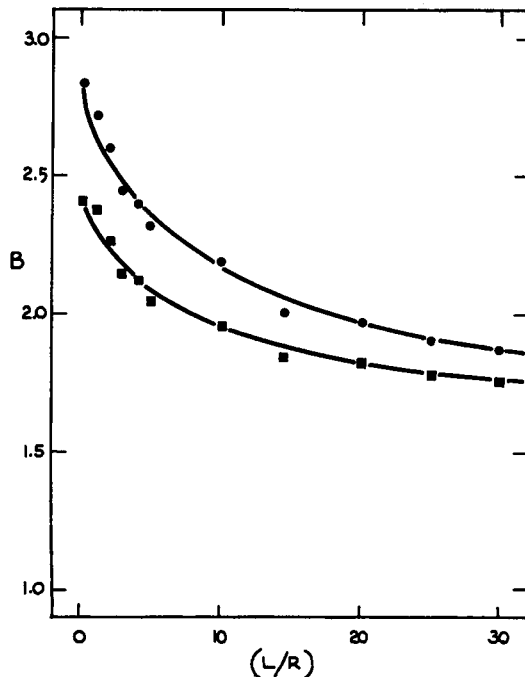


Fig. 4. Swelling index versus capillary L/R for a melt-index-2 polyethylene at two shear rates: (●) $G = 200 \text{ sec.}^{-1}$; (■) $G = 50 \text{ sec.}^{-1}$.

TABLE I

Parameters of eq. (5) Found at 190°C. for a Low-Density Polyethylene of Melt Index 2 at Various Shear Rates. The corresponding end correction and true shear stress at the wall values are also tabulated. The parameters in section I of the Table were computed by setting the end correction $e = 0$ in eq. (5) while the parameters in section II were found by using the observed values of e

$G, \text{sec.}^{-1}$	50	75	100	150	200	
e	3.83	4.29	4.75	5.38	5.92	
$\tau_{tw} \text{ dynes/cm.}^2 \times 10^5$	4.41	5.39	6.20	7.47	8.47	
I	B_0	2.35	2.47	2.54	2.66	2.72
	B_∞	1.74	1.76	1.78	1.81	1.81
	k	1.32	1.90	2.35	3.71	4.74
II	B_0	2.66	2.85	3.01	3.25	3.48
	B_∞	1.74	1.76	1.78	1.81	1.82
	k	1.32	1.90	2.51	3.70	4.83

straight line when plotted against shear stress, as is shown in Figure 5. B_∞ is much less dependent on shear stress, as seen in the same figure.

The most interesting relationship is shown in Figure 6, where k is plotted against shear rate. A straight line passing through the origin can be readily fitted to these points, so that the following relationship can be written:

$$k = (C/4)G \quad (15)$$

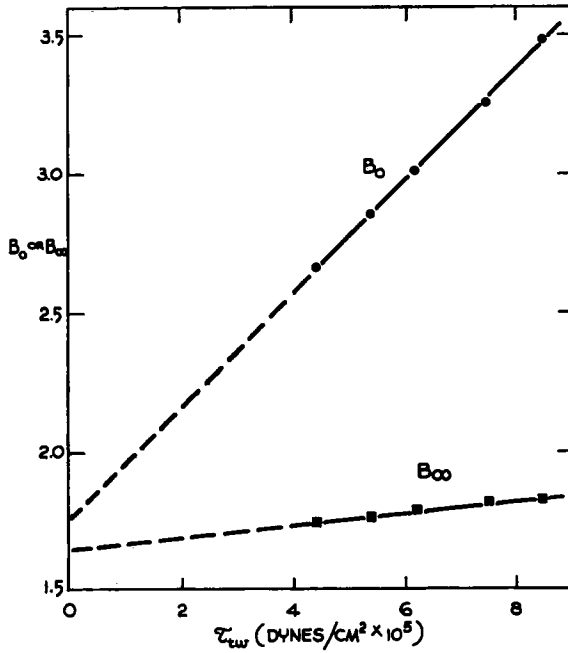


Fig. 5. Variation of B_0 and B_∞ with shear stress.

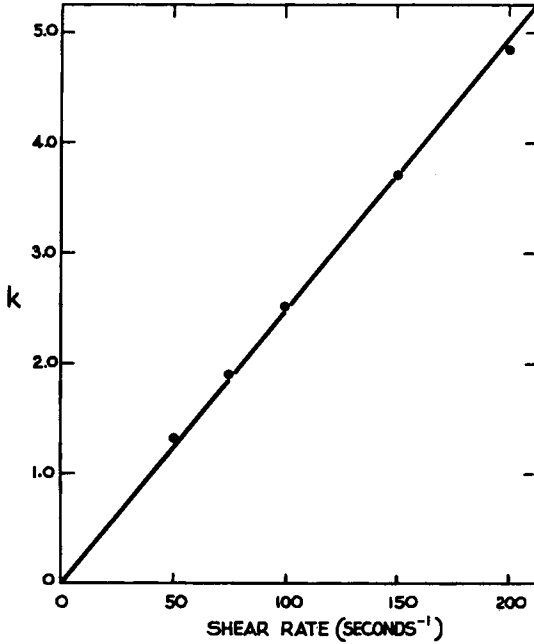


Fig. 6. Variation of k with shear rate.

and hence eq. (5) can be rewritten as

$$(B - B_{\infty}) = (B_0 - B_{\infty}) \exp \{ -C[(L/R) + e] \} \quad (16)$$

Time does not appear explicitly in this equation. The change in extrudate swelling with die length appears to be a purely geometric effect, the decay rate of swelling pressure with die length being independent of shear rate, shear stress, or residence time. (The actual amount of swelling does, of course, depend on shear stress because of the dependence of B_0 and B_{∞} on shear stress.)

Equation (16) can be rewritten in terms of an average shear strain as:

$$(B - B_{\infty}) = (B_0 - B_{\infty}) \exp [-CS/2\sqrt{2}] \quad (17)$$

where the average value of shear strain from eq. (13) is used.

The swelling of an extrudate thus increases with the shear stress and decays exponentially with the shear strain put on the melt system, a result reported to us independently by Hodge and Layton.¹⁷ This result is related to that observed in rotational viscometers, where the degree of elastic recovery is known to depend on total shear strain imposed on the system.¹⁸ In this work the decay of swelling (elastic recovery) has been shown to occur at constant viscosity.

Discussion

As long as only applied pressure, measured output rates, and die dimensions were considered, the viscoelastic behavior of polyethylene in flowing through a capillary seemed to present no basic theoretical difficulty. A viscosity independent of capillary dimensions could be computed and an elastic modulus in agreement with expectations from molecular calculations could be extracted from the data.¹² The extent of molecular deformation could be calculated and there was no reason to suppose that any changes were taking place in the capillary itself. The observed variations of extrudate swelling with increasing capillary length-to-radius ratio therefore suggest that another elastic mechanism is operating on a scale larger than molecular dimensions. The effect of this long-range order could be considered equivalent to the memory effect, referred to particularly by Arai¹ and Clegg.⁴ Prior to extrusion the polymer melt has a certain macroscopic configuration. Postextrusion swelling occurs because the extruded polymer melt is "remembering" the configuration it possessed prior to passage through the die. The importance of total shear suggests a breakdown of this macroscopic structure, although complete accord on this point does not at the moment appear possible. Independent of the interpretation, however, these experiments, as well as those of Tordella,¹⁶ show that changes in elastic strain occur in the capillary.

The concept of macroscopic melt structure can be applied to the consideration of the change in filament distortion with capillary length, indicated in Figures 1, 2, and 3. Melt fracture, which results in filament distortion, occurs at a certain critical value of molecular deformation,¹²

independent of die dimensions. Since the amount of resulting distortion depends on L/R , we can assume that it also depends on total shear strain and hence on the long-range macroscopic melt structure.

In summary, the results show that in studying the viscoelastic properties of polymers the viscosity depends only on the shear stress and shear rate (both independent of die dimensions) but the degree of postextrusion filament swelling depends on both shear stress and shear strain. Melt fracture occurs at a constant value of shear stress (and hence of molecular deformation), independent of die dimensions. The result of the melt fracture process, the degree of filament distortion, depends on the extent of the melt structure, which in turn is a function of total shear strain and hence of die dimensions.

The authors wish to thank Dr. H. W. Holden for helpful discussions, and Canadian Industries Limited for permission to publish this paper.

References

1. Arai, T., *Nippon Gomu Kyokai-shi*, **30**, 993 (1957).
2. Bagley, E. B., *J. Appl. Phys.*, **28**, 624 (1957).
3. Philippoff, W., and F. H. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
4. Clegg, P. L., *The Rheology of Elastomers*, Mason, P., and N. Wookey, Eds., Pergamon, London, 1957, p. 174.
5. Burgess, D., and H. I. Lewis, *Brit. Plastics*, **34** (3), 177 (1961).
6. Kast, W., Lecture held at "Arbeitstagung für Spinnprobleme," Graz., Austria, October 27th, 1961.
7. Middleman, S., and J. Gavis, *Phys. Fluids*, **4**, 355 (1961).
8. Middleman, S., and J. Gavis, *Phys. Fluids*, **4**, 963 (1961).
9. Middleman, S., and J. Gavis, *Phys. Fluids*, **4**, 1450 (1961).
10. Spencer, R. S., and R. E. Dillon, *J. Colloid Sci.*, **3**, 163 (1948).
11. Mooney, M., in *Rheology*, vol. 2, F. R. Eirich, Ed., Academic Press, New York, 1958, p. 196.
12. Bagley, E. B., *Trans. Soc. Rheol.*, **5**, 355 (1961).
13. Hunter, E., and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).
14. *Am. Soc. Testing Mater. D 1233-57T*.
15. Tordella, J. P., *J. Appl. Phys.*, **27**, 454 (1956).
16. Tordella, J. P., *J. Appl. Polymer Sci.*, **7**, 215 (1963).
17. Hodge, C. W., and J. Layton (Imperial Chemical Limited, England), private communication.
18. McCord, R. A., and B. Maxwell, *Mod. Plastics*, September 1961.

Synopsis

When polymers are extruded from a reservoir through a capillary the extrudate diameter is generally greater than the capillary diameter. Experiments with polyethylene show that the extent of this extrudate swelling depends, at constant shear stress, on the length-to-radius ratio of the capillary even though the viscosity does not. Consideration of this result at various shear stresses indicates that the degree of swelling depends on the total shear strain imposed on the melt. The same factor also governs the amount of extrudate distortion observed when melt fracture occurs.

Résumé

Lorsque les polymères sont extrudés d'un réservoir à travers un capillaire, le diamètre d'extrusion est généralement plus grand que le diamètre du capillaire. Les expériences avec le polyéthylène montrent que l'importance du gonflement du produit extrudé dépend, à force de cisaillement constante, du rapport longueur sur rayon du capillaire même lorsque la viscosité n'en dépend pas. L'examen des résultats à diverses forces de cisaillement indique que le degré de gonflement dépend de la tension totale de cisaillement imposée à la masse fondue. Le même facteur régit également l'importance de la distorsion du produit extrudé observée lorsqu'il se passe une fracture de la masse fondue.

Zusammenfassung

Bei der Extrusion von Polymeren aus einem Reservoir durch eine Kapillare ist der Durchmesser des extrudierten Körpers allgemein grösser als der Kapillardurchmesser. Versuche mit Polyäthylen zeigen, dass das Ausmass dieser Verdickung bei konstanter Schubspannung vom Verhältnis der Kapillarlänge zum Radius abhängt, wenn das auch für die Viskosität nicht zutrifft. Das Ergebnis bei verschiedener Schubspannung zeigt, dass der Verdickungsgrad von der gesamten, der Schmelze erteilten Scherungsverformung abhängt. Der gleiche Faktor ist auch für den Betrag der Verdrehung des extrudierten Körpers bei einem Bruch der Schmelze massgebend.

Received June 25, 1962