A Study of Time Dependence of Polyethylene Flow in Capillary Viscometry

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INTRODUCTION

The flow behavior of polyethylene in capillary viscometers is complicated by the non-Newtonian character of the melt. Among the complicating features is the reported occurrence of a critical shear rate,[1-3] above which the extruded filament becomes distorted. Recently, a further complicating feature has been reported. This consists of systematic time drifts in the output rate of polyethylene[4,5] extruding from the melt index apparatus.[6] Similar time drifts in the output rate have been noted in studies of the extrusion behavior of some low density polyethylenes from a gas-operated capillary viscometer. The most marked effect, under certain conditions of fixed temperature and pressure, is a pronounced increase in the output rate of the melt prior to the attainment of steady state extrusion rates. This can persist over periods exceeding 1 hr. In some cases an initial drop in the output rate is also noted. This effect is of shorter duration, however. The time drifts in the output rate of polyethylene thus seem more generally associated with the capillary extrusion of the polymer.

This publication deals primarily with the long-term rise in the output rate. It is intended to indicate the magnitude of the effect, its dependence on extrusion pressure and temperature, its variation with the geometry at the entry of the extrusion die, and so to focus further attention on an interesting extrusion effect which has only recently been explicitly reported. No formal attempt is made to provide a theoretical basis for the observations, but some qualitative arguments are suggested for an interpretation of the data.

EXPERIMENTAL

The rate of polymer flow was measured by use of the gas-operated capillary viscometer previously described by Bagley.[7] The unit was operated over a temperature range of 120–200°C. and could be controlled to about ±0.1°C. at any temperature in this range.

In a major portion of this work a set of tool steel capillary dies was employed in the viscometer. These had a common capillary radius of 0.0921 cm. and an L/R ratio of 2.87. The included angle at the die entry ranged from 180° to 60°. For convenience, the dies are coded D_{180}, D_{160}, D_{120}, D_{80}, and D_{60} to denote dies in which the included angles are 180, 160, 120, 80, and 60°, respectively.

The polyethylenes studied had melt flow indices[6] of 0.3–7. The resins were of the low density type (approx. 0.92 g./cc.), although some high density samples (0.96 g./cc.) were also used in preliminary experiments.

In an experimental run, the viscometer was filled with solid polyethylene which had been stabilized against thermal degradation by the incorporation (by means of milling at 120°C.) of 0.1% by weight commercially available antioxidant (Santonox). A period of 15 min. was sufficient for the polymer to come to thermal equilibrium in the viscometer. The melt was then extruded by applying nitrogen pressure, measured on Bourdon gauges. Consecutive cuts of extrudate were taken over timed periods until the viscometer was emptied. The weighed, timed cuts indicate the extrusion rate. Throughout this procedure, the pressure was maintained constant at the selected value. Depending on the polymer and the extrusion conditions, extrusion times of up to 80 min. could be attained.

RESULTS

Typical output rate versus time of extrusion curves are given in Figure 1. The curves are very similar in character to those obtained by Rudin and Schreiber[5] in extrusion from a melt indexer. The increase in the output rate is quite evident. Zero time is defined as the instant of pressure imposition on the melt. Errors involved in pressure readings, temperature fluctuations, and in timing
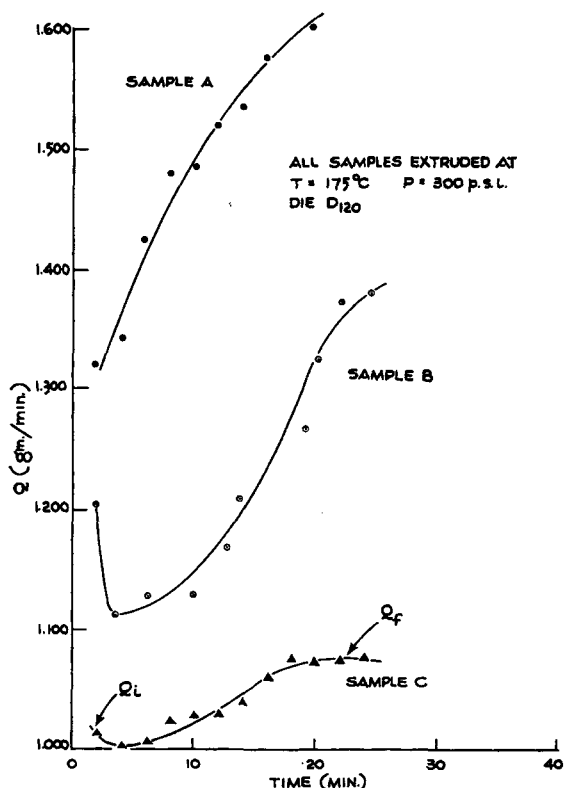
Fig. 1. Typical output rate vs. time of extrusion results for three low density polyethylenes of melt index approx. 0.5.

eter reservoir. Preliminary evidence suggests that high density polyethylenes attain their steady-state output rates more rapidly than low density materials. The initial decrease in the output rates shown by Samples B and C are within the possible experimental error of these determinations. This systematic effect was encountered so frequently at extrusion conditions resulting in higher apparent melt viscosities, both in this work and in extrusion from a melt index apparatus,[6] that it is considered real. It has been discussed more fully in previous publications from this laboratory.[5,8]

The dependence of the increasing output rate effect on several extrusion variables is elaborated below.

(1) Effects of Pressure and Temperature

In general, for a given polymer, the apparent steady-state extrusion rate tends to be attained more rapidly under conditions resulting in lower apparent melt viscosities. It is, however, impossible to generalize about the variation in the overall change in output rates $(Q_f - Q_i)$, with extrusion conditions.

The effect of varying the extrusion pressure is indicated in Figure 2. For convenience, the data are given in terms of the per cent change from the initially measured output value, Q_i. The poly-

and weighing of the extrudate cut can account for a random error in the output rate of about 3%. In all represented cases, the total change in output is systematic and exceeds 7%. The effect can therefore be considered due to sources other than experimental error.

The three low density polyethylenes represented in Figure 1 have roughly similar melt indices of 0.5. The distinct sets of results indicate the time drift effects to be a polymer characteristic. Three quantities can be discussed in connection with the presented data. These are the total change in the output rate, the time required to attain steady-state extrusion and, consequently, the rate of change in the output of polyethylene. The overall rise in the output rate proceeds from an initial value Q_i, towards a higher, presumably steady-state output rate Q_f (see Sample C, Fig. 1). The total change in output rate is usually of the order of 15%, although in some cases a rise of up to 40% has been observed. The steady-state output rate is generally attained only after some 20–60 min. of extrusion, depending on the polymer and extrusion conditions. In some cases (Sample A) the steady state was not attained prior to emptying the viscom-
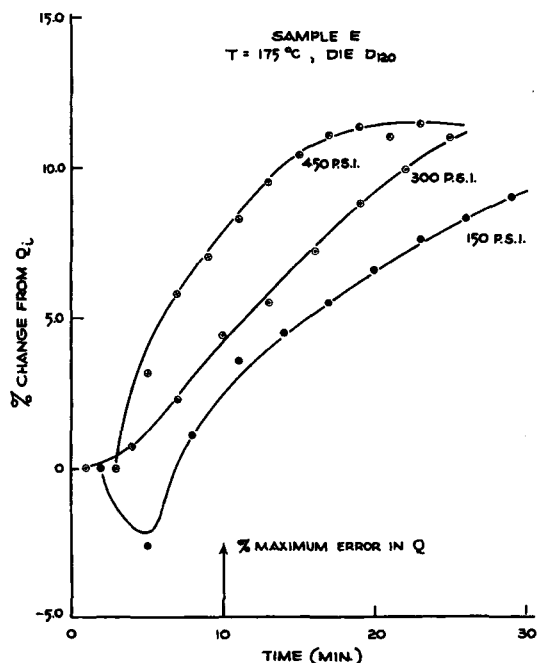

Fig. 2. Effect of extrusion pressure on time dependence of output rate for low density polyethylene Sample E (melt index 0.44).
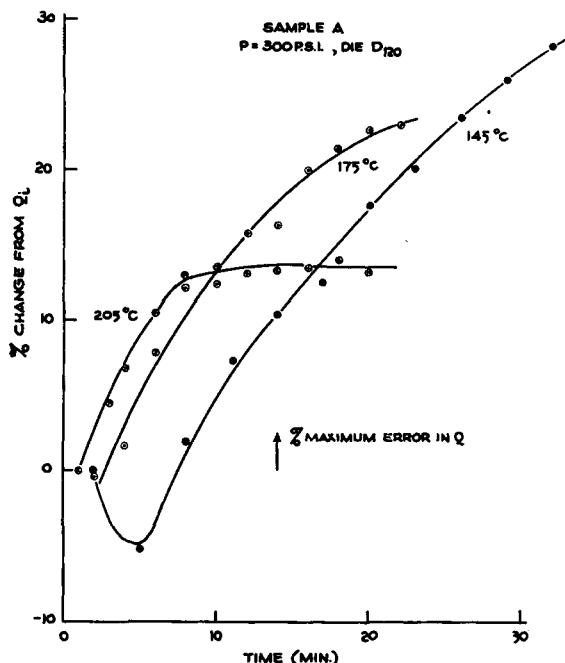
Fig. 3. Effect of melt temperature on time dependence of output rate.

ethylene is a low density specimen of melt index 0.44. Evidently the slope of the output rate–time curve increases with increasing extrusion pressure. The initial drop in output rate is noted, in this case, only at 150 psi. In the data of Figure 2 there also appears to be an increase in the overall change in the output rate with rising extrusion pressure.

The effect of varying melt temperature is shown in Figure 3. Once again, the steady-state output rate is attained most rapidly at 205°C., corresponding to the lowest melt viscosities in this sequence. At the lower temperatures no evidence of steady-state extrusion may yet be seen within the 30 min. of the experimental time. A distinction should be noted between the data of Figures 2 and 3. While an increase in the extrusion pressure also tends to increase the slope of the output rate–time curve, the rate of rise in polymer output is not significantly affected by varying temperatures. The initial decrease in output again is noted only at the lowest temperature in the sequence, corresponding to the maximum melt viscosities of the sample under discussion. In this case, the total change in output rate decreases with rising melt temperature. This is a characteristic of the particular sample, however, rather than a general phenomenon. Once more, in all cases, the magnitude of the change in the output rate is beyond allowances for experimental error.

(2) Effect of Molecular Size

The evident dependence of the time drift in the output rate on apparent melt viscosity suggests a relationship with the molecular dimensions of the polymer specimen. In this work, only unfractionated samples were employed, and no direct evaluations of molecular weight were available. There is, however, a general proportionality between the melt index of polyethylene and its melt viscosity.[b] Since the melt viscosity can, in turn, be considered a function of the molecular weight of the polymer,[10] the melt index may be regarded as a crude indication of the average molecular size of the sample.

The variation in the total change of output rate for a series of low density polyethylenes having melt indices of 0.1–4.0, is shown in Figure 4. The semilogarithmic plot indicates that the effect is more pronounced for low melt index (high molecular weight) resins. Resins with melt index exceeding about 1.0, did not, as a rule, display significant variations in output rate in this extrusion system.

(3) Effect of Die Geometry

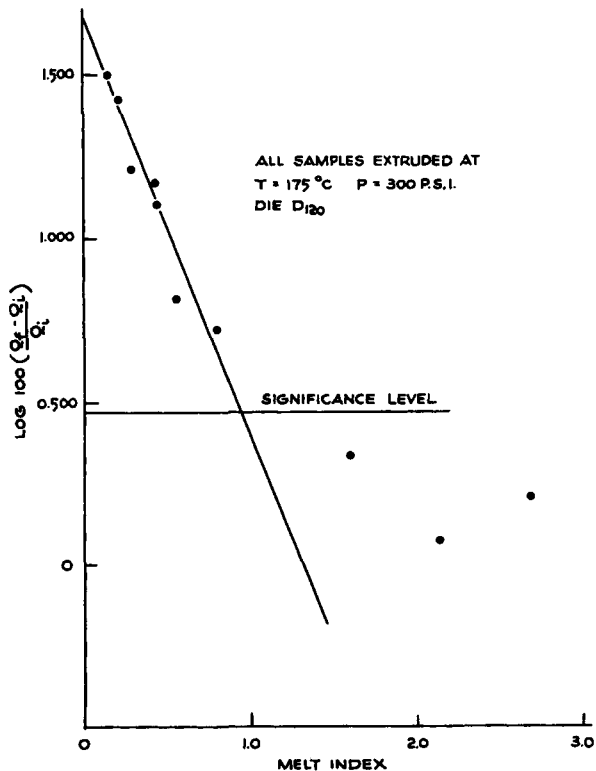The flow behavior of polymer melts is known to depend on the die entry angle.[2,11,12] A brief

Fig. 4. Dependence of total change in output rate of polyethylene on melt index of specimen.
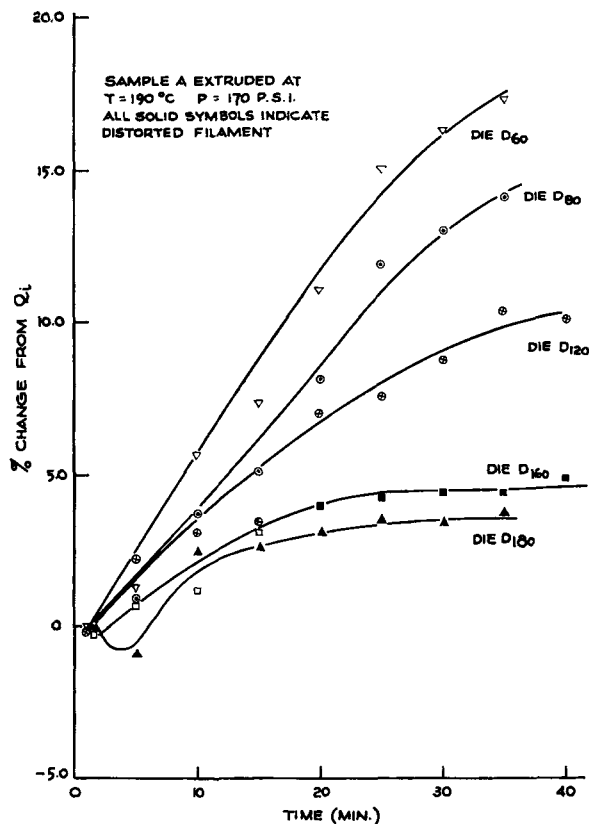
Fig. 5. Effect of die entry geometry on time dependence of output rate of polyethylene Sample A.

study of the effect of changing the die entry angle on the time dependence of output rate was therefore carried out. The polyethylene Sample A was extruded at 170 psi and 190°C. through dies D_{180}–D_{60}. The results are given in Figure 5.

The three most highly tapered dies (D_{60}, D_{80}, and D_{120}) produce the most notably time-dependent output functions. It is noteworthy that with these dies, smooth extruded filaments were obtained over the entire extrusion period.

The data for die D_{160} are particularly interesting. The filament initially appeared smooth, and some rise in the output rate is noted to the 20-min. mark. The extrudate, however, became distorted at about the 16–17-min. mark. Thereafter, as shown in Figure 5, the output rate of the distorted filament remained constant within the expected error of determination. The use of the flat entry die, D_{180}, led to distorted extrudates from inception of the experiment. The initial drop in the output rate in the appropriate curve of Figure 5, is similar to those remarked upon previously. Beyond this, however, the output rate is again approximately constant. The time-dependent rise in the output

rate then, seems associated with undistorted filament extrusion and appears to be more pronounced when more steeply tapered dies are employed.

In all cases shown in Figure 5, initial output rates were nearly constant (0.58 ± 0.03 g./min.). The small differences were probably due to slightly different die radii.

DISCUSSION

The magnitude and duration of the apparent time effect described above, is somewhat surprising. The reality of the effect was therefore subjected to a number of tests.

Repeat determinations, even with previously extruded polymer samples, consistently reproduced entire output rate versus time curves to better than 5%. The rise in the output rate was therefore reconfirmed as experimentally significant.

It seemed possible that the effect could be due to lack of temperature equilibrium in the body of the melt. In a number of trials the initial warm-up time was therefore extended from 15 to 45 min. prior to the initiation of extrusion. Typical results are given in Figure 6. The additional pre-
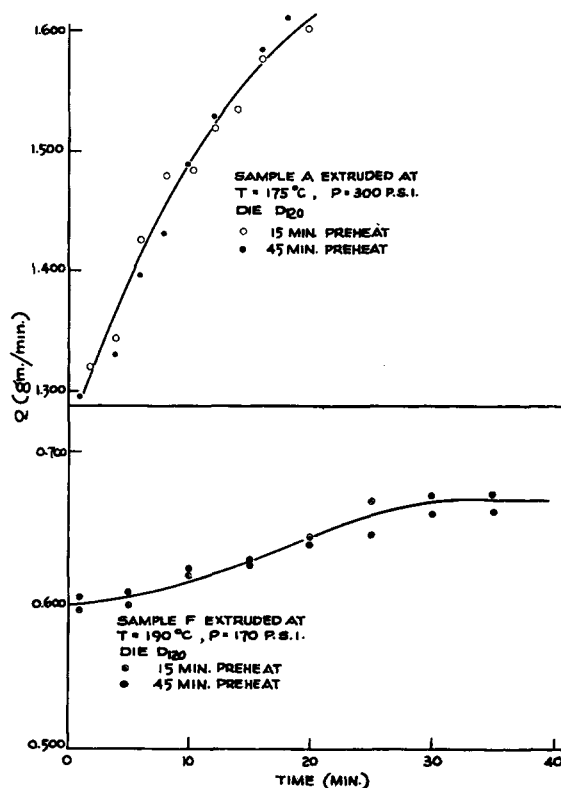

Fig. 6. Effect of extended preheating on the time dependence of output rate in polyethylenes.

heating time evidently produced no significant change in the output–time curves. It seems reasonable to conclude that the phenomenon is not an artifact of nonequilibrium thermal conditions in the viscometer reservoir.

The presented data indicate that under certain extrusion conditions, some polyethylene melts respond very slowly to the sudden imposition of an extrusion pressure. The overall time drift in the output rate appears to be identifiable with at least two distinct phenomena. One is the initial decrease in output rate, noted especially at higher apparent melt viscosities; the other is a rise in the output rate toward a steady-state value which persists over long time periods. The shape of the output rate–time curves is closely analogous with those obtained in extrusion from the melt indexer.[5,8] The experiments described by Rudin and Schreiber[8] strongly suggest that the initial decrease in the output rate is the result of an elastic response of the melt following sudden pressure imposition. A similar mechanism is suggested to account for the observations noted here.

The long-term rise in the output rate may reflect a time-dependent rise in the effective shear stress on the melt, a diminishing melt viscosity, or a combination of the two factors. An argument of increasing shear stress due to frictional heating of the melt was used by Marker, Early, and Aggarwal[4] to describe the rising output rate from a melt index apparatus. Rudin and Schreiber[8] showed this postulate alone to be inadequate to account for the observed results. An alternate mechanism of increasing shear stress can be envisaged. The effective stress, τ_e, may be defined by the equation[7]

$$\tau_e = P/2[(L/R) + n] \qquad (1)$$

where P is the applied pressure, L and R are the length and radius of the die, and n is an end correction term, occasioned in part by melt elasticity and by the viscous resistance to the liquid flowing through a capillary. A time-dependent rise in the shear stress would imply that the end correction decreases from some initial value to a steady-state value characteristic of the polymer and of the extrusion system. In this event, the time dependence in output rate should be much reduced when the length of the capillary becomes large compared with the correction value n.

The effect of varying the L/R die ratio on the time drift in output rate was briefly examined. The polyethylene B was extruded at 190°C. through the die D_{180} ($L/R = 2.87$), and through another
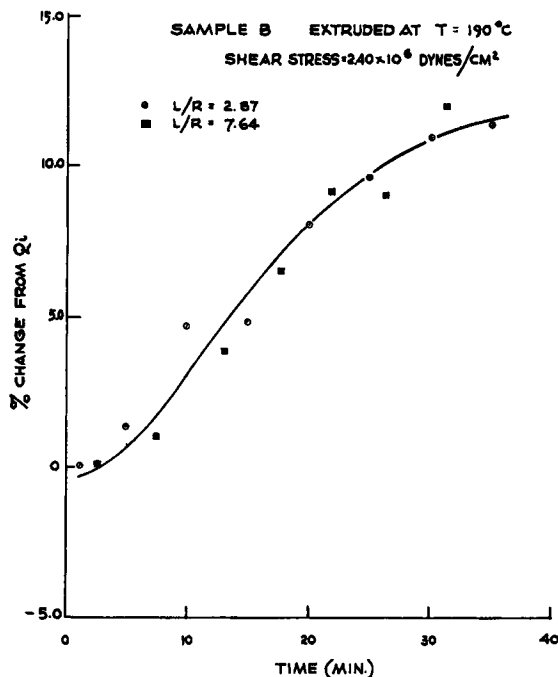

Fig. 7. Effect of changing L/R ratios of extrusion die on time dependence of output rate.

flat-entry die with $L/R = 7.64$. The extrusion pressures were set so as to produce the same shear stress on the polymer (2.40×10^6 dynes/cm.²), n being assumed to be zero. Comparison of the data was complicated by the inequality of the radii of the two dies, but the following may be noted. The initial output rate with the longer die was about 2.10 times the initial rate with D_{180}. The viscometer reservoir (filled to capacity in both cases) was exhausted in about 35.5 min. with D_{180} and in 16.0 min. with the longer die. The flow time ratio of 2.21 is in good agreement with the ratio of initial output rates. This indicates that the output rate–time relationships in the two cases ran a parallel course. In order to compare the data on the same time scale, the time of extrusion results pertaining to the $L/R = 7.64$ die were multiplied by 2.15 (the average of 2.2 and 2.1), and the data plotted in Figure 7. As a good approximation, the per cent change from Q_i versus time plot in the two cases is identical, although the contribution to a postulated changing shear stress due to a change in the end correction has been altered by a factor exceeding 2.

While the postulate of increasing shear stress cannot be entirely dismissed in a consideration of the rising output rate phenomenon, the above experiment indicates it to be of secondary impor-

tance. More substantial progress can be made in analyzing the results from a viewpoint of decreasing melt viscosity.

The melt viscosity has been defined by the equation[18]

$$\eta = F(Z_w)/J(\phi, T) \qquad (2)$$

where F is a statistical coordination factor dependent on Z_w, the weight-average number of atoms constituting the polymer chain, and J is a segmental jump frequency dependent on a segmental free volume ϕ and the temperature T. A decrease in the melt viscosity can be due to an increase in the jump frequency, or a decrease in the statistical factor.

The segmental jump frequency could be increased by a rise in the effective melt temperature. Recent results obtained in this laboratory show that the temperature of polyethylene entering the die orifice in the gas operated viscometer used in these experiments does indeed rise following a pressure increase. A steady-state melt temperature is, however, attained within 1–2 min. following pressure imposition, so that the duration of the rising output rate phenomenon cannot be explained by temperature changes in the melt.

The most self-consistent interpretation of the rising output rate at given pressure stems from the assumption of a time-dependent decrease in the statistical factor F of eq. (2). In the extruding melt, a gradual alignment of the polymer chains in the direction of flow can be postulated. There is a consequent shift in the segmental entanglement-disentanglement equilibrium towards a state of relative disentanglement, and this tends to decrease the statistical factor. It is immaterial to this discussion whether the lowering of F is accomplished by a decrease in the number or by a lowering of the efficiency of segmental entanglements. The rising output rate from the viscometer is thus identified with configurational changes occurring in the body of the melt. The data are qualitatively consistent with this view.

Effect of Extrusion Pressure. The segmental entanglement-disentanglement equilibrium might reasonably be expected to shift towards progressive disentanglement as the pressure imposed on an extruding melt initially at rest increases. Similarly, the rate of decrease in the statistical factor (and, therefore, in the melt viscosity) would vary with the magnitude of the imposed pressure. These postulates are consistent with the data of Figure 2.

Effect of Melt Temperature. It is generally stated[13] that the statistical factor of eq. (2) is independent of temperature. At given extrusion pressure, the rate of decrease in F should then be independent of temperature. By this reasoning, the rate of increase in the output of polyethylene should also be independent of temperature. This is in keeping with the results of Figure 3.

Effect of Die Entry Geometry. The results of Figure 5 show the slopes of the output rate–time curves to increase as the included die entry angle decreases. At first, this appears to contradict the postulated link between the rising output rate and configurational changes occurring in the bulk of the melt. Recently, however, Bagley and Birks,[14] using a transparent viscometer, have shown that the geometry at the die entry has a very marked effect on the flow pattern established in the body of the extruding melt. A decrease in the included die entry angle speeds the establishment of a steady-state flow pattern. The results of Figure 5 therefore suggest that steepening the die entry taper also promotes those configurational changes in the melt which lead to the establishment of steady-state flow conditions.

Elastic Flow Turbulence. The configurational changes leading to the decrease in the statistical factor are postulated to be the result of orientation of the polymer chains in the direction of flow. The occurrence of elastic turbulence at the die entry will offset this orientational tendency, so reducing the magnitude of changes in the statistical factor. This would account for the virtual disappearance of the rising output rate effect in the extrusion of distorted filaments, as shown in Figure 5. The persistence of the initial drop in the output rate in the extrusion of distorted filaments also suggests that this effect is distinct and independent of the long-range rise discussed in this article.

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Synopsis

It is known that polyethylene extruding from a capillary viscometer does not attain a steady-state output rate immediately following a pressure imposition. The time dependence of output rate was studied quantitatively, and under some extrusion conditions was found to be of surprisingly large magnitude. The most notable effect is an overall rise in the output rate; its magnitude and duration depends on the extrusion pressure and temperature and on the entry geometry of the die employed. The magnitude of the effect is also characteristic of particular polyethylene samples and seems associated with smooth filament extrusion of the polymer. The steady-state output rate can exceed the initial rate by as much as 40%. The rising output rate characteristic has been associated with a decreasing melt viscosity. This is taken to be the result of configurational changes occurring in the extruding melt. The data are shown to be qualitatively consistent with this postulate.

Résumé

On sait que de polyéthylene sortant d'un viscomètre à capillaire n'atteint pas immédiatement une vitesse d'extrusion stationnaire dès après l'application d'une pression. Le dépendance du temps vis-à-vis de la vitesse d'extrusion, étudiée quantitativement, a montré que dans certaines conditions d'extrusion, elle était d'une ampleur surprenante. L'effet le plus remarquable est une augmentation généralisée de la vitesse de sortie; son ampleur et sa durée dependent de la pression d'extrusion et de la température ainsi que de la géométrie de l'ouverture de l'appareil utilisé. L'importance de l'effet est aussi une caractéristique des échantillons particuliers de polyéthylene utilisés et semble être associée à la sortie du polymère en filaments. La vitesse stationnaire de sortie peut dépasser la vitesse initiale de 40%. On a associé la caractéristique de l'augmentation de vitesse à une diminution de la viscosité de la masse fondue. On admet que ceci est dû à une modification configurationnelle au sein du polymère. On montre que les résultats confirment qualitativement le postulat.

Zusammenfassung

Es ist bekannt, dass Polyäthylen bei der Extrusion aus einem Kapillarviskosimeter nicht unmittelbar nach einer Druckanwendung eine stationäre Austrittsgeschwindigkeit erreicht. Die Zeitabhängigkeit der Austrittsgeschwindigkeit wurde quantitativ untersucht und es wurde gefunden, dass sie unter gewissen Versuchsbedingungen überraschend gross war. Der bemerkenswerteste Effekt ist eine allgemeine Zunahme der Austrittsgeschwindigkeit, ihre Grösse und Dauer hängt von Extrusionsdruck und -temperatur sowie von den geometrischen Verhältnissen an der Eintrittsöffnung des verwendeten Apparates ab. Die Grösse des Effekts ist auch für individuelle Polyäthylenproben charakteristisch und scheint mit einer Extrusion des Polymeren in glatten Fasern zusammenzuhängen. Die stationäre Austrittsgeschwindigkeit kann um bis zu 40% höher liegen als die Anfangsgeschwindigkeit. Das charakteristische Verhalten mit steigender Austrittsgeschwindigkeit wurde zu einer Abnahme der Schmelzviskosität in Beziehung gesetzt. Es wird angenommen, dass diese das Resultat von Konfigurationsänderungen ist, die während der Extrusion in der Schmelze auftreten. Es wird gezeigt, dass die Ergebnisse mit diesem Resultat in qualitativer Übereinstimmung stehen.