LETTERS TO THE EDITORS

Some Elastic Effects in the Capillary Extrusion of Polyethylene

Molten polyethylene is known to be capable of storing elastic strain energy during flow. Most studies of this phenomenon involve the use of apparatus other than capillary viscometers.[1] In the experiments recorded here, the apparent viscosity during capillary extrusion did not respond instantaneously to abrupt changes in shearing stress. These observations, which can be explained in terms of changes in the segmental free volume of the melt, are reported for their inherent interest and because they indicate that the elasticity of flowing polyethylene can some-- times complicate the interpretation of capillary viscometer data.

The apparatus used was the familiar melt indexer,[2] which is a dead-weight plastometer consisting of a heated cylinder within which a weighted piston forces molten plastic through an orifice at the lower end of the cylinder. The polyethylenes studied were natural resins compounded with 0.1% of a commercial antioxidant.

Weights of consecutive, timed outputs of four low-density polyethylenes extruded through a standard melt index die (diameter 0.0825 in., length 0.315 in., included entry angle 180°) under a dead weight pressure of 43.6 psi at 190°C are plotted in Figures 1 and 2. The zero on the time axis in each graph is the moment at which extrusion was started by placing the weight of the melt indexer on the piston. The weight of each extrudate is plotted against the midpoint of the time interval during which it was collected. In each case the polymer was allowed to come to thermal equilibrium before extrusion began. The solid lines in Figures 1–2 connect consecutive outputs immediately after the standard weight was placed on the piston. This is the normal procedure for measuring melt index,[2] except that the output during the first 6 min. of extrusion is not usually retained. These curves show that the polyethylenes did not reach a steady flow rate immediately on application of the load. The flow rates decreased to a minimum reached about 10 min. after initiation of extrusion. Within our experience, most of the change takes place in the first 6 min., so that the accuracy of melt index measurements is apparently not seriously affected.

The dashed curves in Figures 1 and 2 show the behavior of the same polyethylenes upon release of an excess load. The experimental procedure differed from that described above only in that the piston was driven down 1 in. by an excess load just as the normal weight was placed on it. Depression of the piston required less than 30 sec. When the excess pressure was released, the polymer was ostensibly flowing under the normal load used in the foregoing experiments, but the polymer flow rates were low at first and gradually increased to levels not significantly different from the steady rates reached after a change from no stress to the normal load. The times to reach steady flow rates were slightly longer when the normal load replaced an excess load than when it followed zero load. The good agreement between replicate measurements of timed outputs is indicated in Figures 1b and 2a.

Replicate experiments in which the viscometer was loaded with polyethylene granules and with compression-molded plugs which just fitted the cylinder showed that the effects observed were not caused by air bubbles in the melt. The flow behavior was the same in both cases, and is shown as the solid curve in Figure 2a.

The curves in Figure 3 show that the effects described above reflect the manner in which the normal load is reached. Polyethylenes B and C were extruded, in this case by sudden application of the normal load. The initial decrease
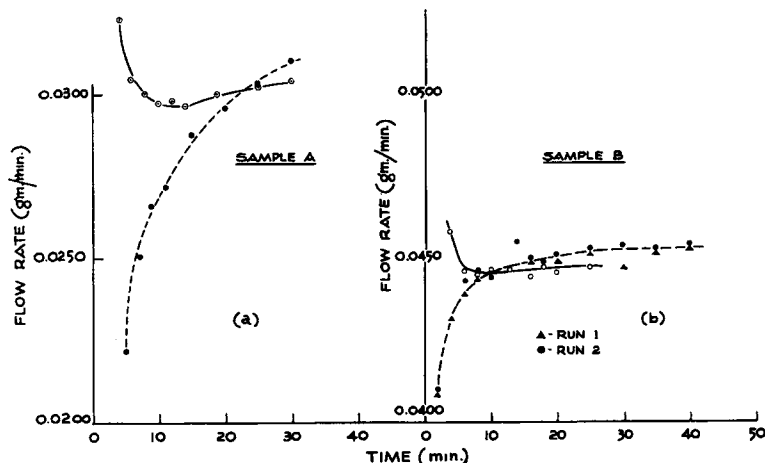

Fig. 1. Flow rate vs. time since application of dead-weight load: (———) consecutive outputs immediately after weight placed on piston; (- -) outputs on release of excess lead. Samples A and B are low-density polyethylenes.
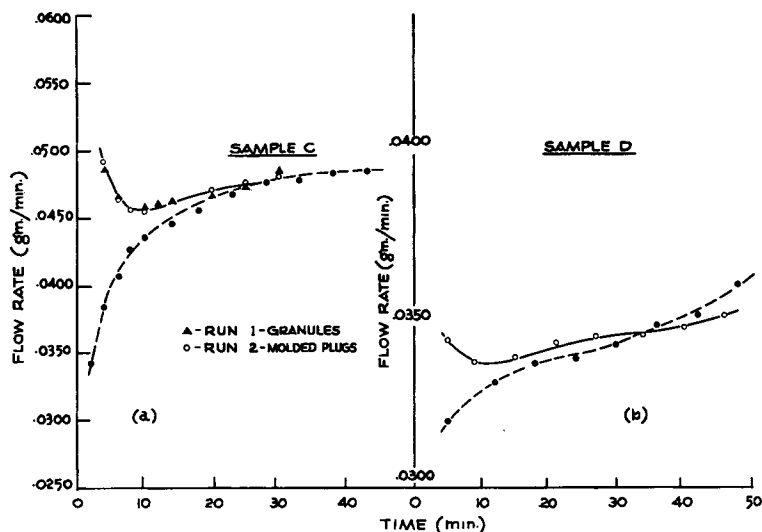
Fig. 2. Flow rate vs. time since application of dead-weight load: (——) consecutive outputs immediately after weight placed on piston; ⚬-) outputs on release of excess load. Samples C and D are low-density polyethylenes.
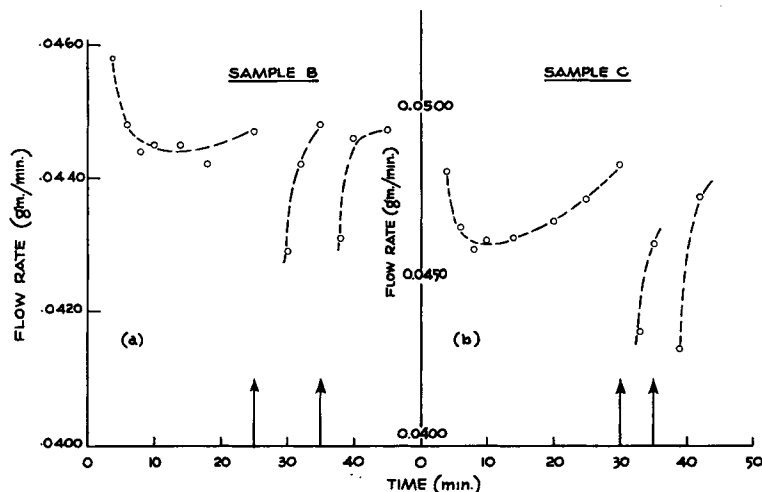
Fig. 3. Effect on flow rate of arriving at standard load from zero load and from excess load. Arrows indicate times at which excess pressure was applied.

of successive output rate measurements followed the expected course. When the initial adjustment in output rate had apparently ceased, the piston was quickly driven down 1 in. and released. Subsequent flow rates were low at first and increased towards the original levels in the manner expected from the behavior of the same polymers in Figure 2. The times to return to steady state flow in this case are shorter than when excess pressure was applied at the start of the extrusion process. This is reasonable, since the melt is denser before the excess compression.

The foregoing observations imply that the apparent viscosity responded gradually to sudden changes in the load on the melt. The primary data were obtained as output rates at constant shear stress and are, of course, related inversely to the apparent viscosity of the polymer. The melt viscosity has been postulated[3] to be determined by the ratio

of a statistical coordination factor F to a segmental jump frequency J, i.e.,

$$\eta = F(Z_w)/J(\phi,T) \tag{1}$$

F depends on the weight-average number of atoms in the chain, Z_w. J is a function of the temperature T and segmental free volume ϕ.

An abrupt change in the pressure on the melt apparently results in a relatively slow response of the free volume ϕ. The gradual decrease in flow rate after application of a load to the stationary melt is assumed to reflect the time-dependent reduction of ϕ which results in increasing viscosity, according to eq. (1). When the standard load replaces an excess load, on the other hand, the polymer is subject to the standard shear stress while its segmental free volumes ϕ still reflects the preceding higher stress.
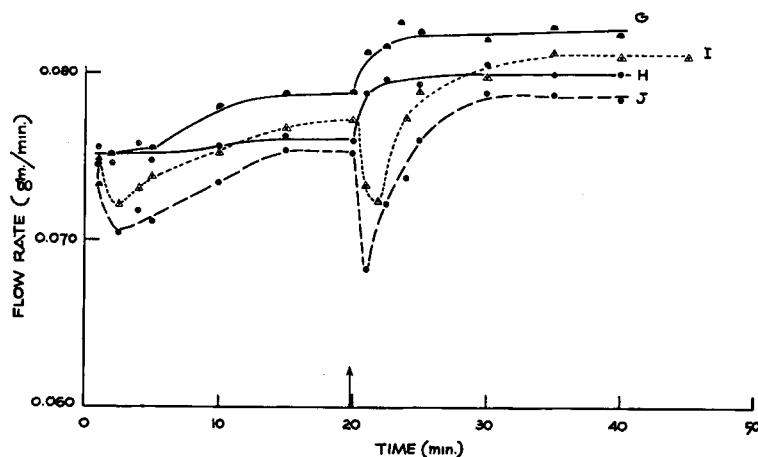
Fig. 4. Flow rate vs. time since start of extrusion of polyethylene samples: (G, H) High-density, linear polyethylenes; (I, J) low-density polyethylenes. Arrow indicates time at which excess pressure was applied.

The result is an initially high viscosity which decreases as the melt expands elastically.

The increasing outputs following the minima shown in the upper curves in Figures 1–3 are more likely associated with a gradual reduction in the effectiveness of chain entanglement and alignment of the polymer chains along flow lines into the orifice.[4] This would tend to reduce F, resulting in a decreased viscosity.

The effects of polyethylene type were investigated, briefly, with the results given in Figure 4. The study included two low-density polyethylenes (dashed curves) and two high density polyethylenes (solid curves). Polymer flow rates were measured from application of the normal load until a steady flow rate had apparently been reached. An excess load was applied to drive the piston down 1 in., the extra load was released, and measurement of output rates was continued. The low-density polymers exhibited the same behavior as similar materials in preceding examples but the linear polyethylenes behaved quite differently. A decrease in output when the load was first applied was not detected. Application and removal of an excess load resulted in increased outputs, which persisted at their higher levels. Evidently the linear polyethylenes had a lower capacity for storage of elastic strain energy then the branched resins.

In the operation of extrusion viscometers the volume swept out by a piston is often equated to the volume of polymer extruded, assuming that the melt is essentially incompressible. The foregoing data indicate that this practice can sometimes be misleading and that the errors involved will probably depend on the extrusion system, temperature, shear rate, and polymer. Marker, Early, and Aggarwal[5] have made this assumption in an interesting recent paper which also reports a time drift in output rates from a melt indexer. This effect is ascribed to frictional heating of the polymer between the piston and cylinder wall. We intend to discuss this alternate way of interpreting time drifts in rates of shear in a forthcoming publication.

References

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H. P. Schreiber
A. Rudin

Canadian Industries Limited
Central Research Laboratory
McMasterville, Quebec, Canada

The Second-Order Transition Phenomena in Polyethylene

Many values have been suggested for the second-order transition temperature of polyethylene by different authors, but none of these has discussed which value is the true second-order transition point and what the nature of the other points is.

We have conducted some dilatometric measurements on polyethylene in the temperature range from -76 to $+28°$ C., using n-propyl alcohol as the filling liquid. Some of our results can be used for discussing the present problem.

The difference between the specific volume of quenched Marlex 50/15 (M_q) and that of annealed Marlex 50/15 (M_a) is shown in Figure 1. It is seen that this value does not