Further Remarks on Time Effects in Capillary Flow of Polyethylene

In previous publications[1-3] we have discussed a time dependence of apparent melt viscosity which is observed under certain conditions during the capillary extrusion of polyethylene. The most pronounced manifestation of this dependence is a gradual rise in the output rate at fixed temperature and applied pressure, from an initial to a higher, steady-state value. The time dependence was found to be a definite polymer characteristic and was assumed to result predominantly from a gradual disentanglement of the polymer chains under the influence of applied stress.

Recently, Skinner[4] has drawn attention to two factors which can affect rheological measurements, particularly in capillary extrusion systems with small reservoir-to-die diameter ratios and with dies having small length-to-diameter ratios. First, as the reservoir is emptied at fixed applied pressure, the pressure drop across the die rises, tending to lower the apparent melt viscosity. Skinner[4] calculated that under extreme circumstances, a 50% increase in the output rate was possible. Second, frictional heating of melt between the plunger or ball bearing of the capillary viscometer and the reservoir wall, first noted by Marker and co-workers,[5] also tends to result in an increase in effective applied stress and in output rate. We have already considered the possible influence of these factors on our observed time dependence results;[3] while they undoubtedly contribute to the rising output rate, and their presence should be considered in the interpretation of rheological data, the overall effect is still primarily a polymer characteristic and appears to be interpretable by our previous arguments.[1-3] In this note we present new data which further support and extend our previous conclusions.

A brief examination has been made of the time dependence of output rate in polyethylene extrusion when the melt is subjected to periodic stress applications. As in the previous experiments, the viscometer was that described by Bagley,[6] having a melt cavity of 1.6 cm. diameter and about 21.5 cm. in length and a capacity for about 30 g. of polyethylene. The flat entry die (D_{180} of ref. 1) had a length-to-radius ratio of 2.87 and a radius of 0.0921 cm. Three low-density polyethylenes with melt indices near 0.5 were involved, and the usual precautions against thermal degradation were observed.

Figure 1 illustrates data typical of the first sequence of runs. Zero on the time axis represents the moment at which stress was first applied to the melt. The solid lines joining open symbols represent the change in flow rate when the extrusion pressure was continuously maintained. The broken lines joining filled-in symbols represent intermittent stress application. In these runs, following each 2-min. extrusion cycle, the pressure was rapidly blown off and the melt was maintained at zero applied pressure for about 5 min. The continuous stress results are similar to our previously reported data; in the shown cases a steady-state output rate is attained after about 30 min. of flow. Intermittent stress application, on the other hand, almost completely removes the time-dependent rise in output rates. The melts therefore may be supposed to relax in the 5 min. periods at zero stress and revert to their randomly oriented, entangled states. Results very similar to those given in Figure 1 have recently been reported by Pohl and Gogos,[7] who studied intermittent shear effects on polyisobutylene

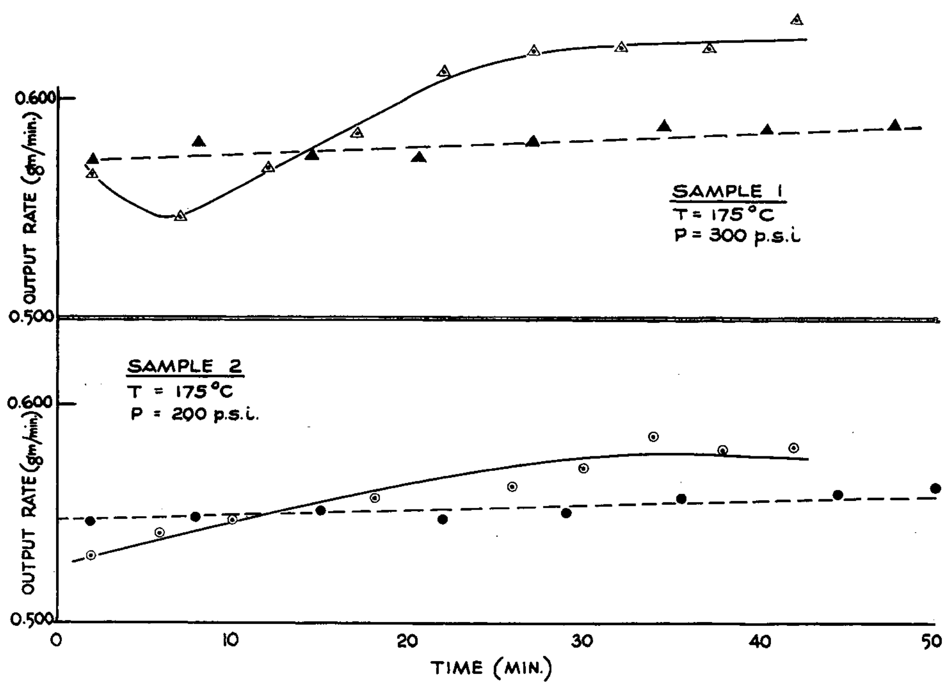

Fig. 1. Time dependence of output rate in polyethylene extrusion: (—) continuous stress application; (--) intermittent stress application.

TABLE I
Effect of Pressure Fluctuations on Time Dependence of Output Rate for Polyethylene Sample 3 (Extrusion at 175°C.)

Experiment A

Time after first pressure imposition, min.	Output rate, g./min., At 300 psi	Output rate, g./min., At 150 psi
1	1.092	
3		0.336
4	1.120	
6		0.344
7	1.127	
9		0.343
10	1.150	
12		0.349
13	1.162	
15		0.356
16	1.180	
18		0.355
19	1.196	
21		0.356
22	1.209	
24		0.353
25	1.211	
27		0.356

Experiment B

Time after first pressure imposition, min.	Output rate, g./min., At 400 psi	Output rate, g./min., At 200 psi
0.5	1.867	
1.5		0.539
2.0	1.925	
3.0		0.553
3.5	1.957	
4.5		0.559
5.0	2.004	
6.0		0.554
6.5	2.030	
7.5		0.560
8.0	2.073	
9.0		0.557
9.5	2.087	
10.5		0.557

melts in a biconical rheometer. The data in Figure 1 again indicate the distinctive polymer characteristic of the time-dependent increase in output rate. However, the results cannot be attributed to the effects described by Skinner.[4] Both in intermittent and continuous shear experiments, the viscometer reservoir is being exhausted and, consequently, if the time dependence were the result of increasing pressure drops across the capillary die it would have to be observed during both methods of operation.

In a second sequence of experiments, continuous extrusion was studied under applied pressures which cycled systematically between two finite levels. Typical data are given in Table I. In experiment A, pressure was alternated between 300 psi (for 1 min.) and 150 psi (2 min.), while in B the cycle was 400 psi ($^1/_2$ min.) and 200 psi (1 min.). The time drift at each of the higher applied pressures is unmistakable, while at the respective lower pressures a minor rise is initially noted but after a few cycles the output rate remains constant. Once again the results are consistent with the hypothesis of slow changes in melt configuration under applied stress.[1] In terms of extrusion at the respective higher stresses, the short residence times at lower but finite stress are not sufficient to counteract tendencies to disentanglement and chain orientation, which are suggested as necessary for the establishment of steady states. The output rates therefore rise, and the periods necessary to the attainment of steady states appear to be longer than when higher stresses are continuously applied. On the other hand, in terms of extrusion at the lower stresses the residence times at higher stress promote the establishment of steady states with a consequent reduction in the duration of the time-dependent increase in output rates.

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A Reply to Skinner's "Polymer Rheology"

Mr. Skinner is to be commended for his letter[1] pointing out a little appreciated source of error in the melt flow index test, namely, the resistance to flow in the reservoir. His analysis of the magnitude of the correction is right, but we disagree with his remark that his example represents an extreme. Further, we prefer to differ with him on his conclusion regarding the error connected with the friction between plunger and barrel. We suggest here practical answers to both of these problems.

We have made actual measurements of the resistance caused by the plastic in the cylinder for materials having much higher n values than the example given by Skinner. We define n:

$$n = \frac{d\,[\log\,(4Q/\pi r_c^3)]}{d\,[\log\,(P_c r_c/2L_c)]} \tag{1}$$