Effect of Processing on Flow Properties of Some Linear Polyethylene Resins

R. W. FORD, R. A. SCOTT, and R. J. B. WILSON, *Research and Development Laboratory, Dow Chemical of Canada, Limited, Sarnia, Ontario, Canada*

Synopsis

Changes in flow properties of polyethylene resins have often been observed during processing operations. Studies in this laboratory show that melt viscosity of polyethylene normally increases when the resin is heated in a compression mold at temperatures below 300°C. At the same time, the solution viscosity actually decreases in some cases. During extrusion, on the other hand, both melt viscosity and solution viscosity are shown to decrease. In addition, the logarithm of melt flow rate is seen to deviate markedly from the expected linear dependence on reciprocal of absolute temperature. The results suggest that both crosslinking and chain-scission reactions occur during processing, the former predominating at low or zero shear, the latter at high shear.

INTRODUCTION

When linear polyethylene is subjected to heating and mixing during fabrication, changes in flow properties are usually observed. Such changes are of practical concern, since most fabricators re-use scrap material in their operation and changes in properties can upset the molding or extrusion process. Even subtle changes in the polymer may lead to problems in fabrication and end use properties.

The nature of such changes in linear polyethylene has received very little attention. In one of the few publications on the subject, Heitmiller et al.[1] suggested that an observed increase in melt viscosity on extrusion could be attributed to improved mixing of polymer molecules of different molecular weights. These authors claimed no change in solution viscosity for their samples on extrusion and hence discounted changes in average molecular weight. More recently, Pritchard et al.[2] reported that Phillips-type linear polyethylenes may undergo crosslinking during processing, leading to an increase in melt viscosity at low shear rates. This tendency to crosslink can be eliminated, according to these authors, by elimination of unsaturation from the polymers.

Over the years, observations in this laboratory have repeatedly shown changes in melt index due to molding and extrusion. In many cases an increase in melt viscosity has been accompanied by a decrease in solution viscosity. In this paper, data are presented which illustrate the effects of heat and shear on some linear polyethylenes.

EXPERIMENTAL

Polyethylene Samples

A total of eleven polyethylene samples have been studied, representing five different types of polymers. Ten samples were typical Ziegler polymers, while the eleventh was a Phillips-type resin. Table I contains pertinent information on each sample.

TABLE I

Sample number[a]	Melt index, dg./min.	Resin type
A-1	4.07	0.940 g./cc. density ethylene–butene-1 copolymer
B-1	0.53	0.950 g./cc. density ethylene–
B-2	0.25	butene-1 copolymer
C-1	0.40	0.950 g./cc. density ethylene–
C-2	0.33	butene-1 copolymer
C-3	0.36	
C-4	0.53	
D-1	0.86	0.960 g./cc. density ethylene
D-2	0.85	homopolymer
D-3	0.55	
E-1	0.84	Phillips-type 0.960 g./cc. density ethylene homopolymer

[a] Series A and series B samples were produced with a different catalyst system from that used for resins in series C and series D.

Procedure

Extrusions were carried out in a 1-in. Killion extruder with a length/diameter ratio of 24/1. A metering-type screw with 3/1 compression ratio and a flight depth of 0.050 in. in the metering zone was used throughout. Screw speed was continuously variable from 20 to 135 rpm.

Compression moldings were made using a Pasadena Hydraulics press fitted with electrically heated platens, a $\frac{1}{16}$ in. thick steel picture frame mold between two ferrotype plates, and suitable parting sheets. At temperatures below 220°C., Mylar film was satisfactory, but at higher temperatures aluminum foil was used. Moldings were quenched in ice water and subsequently chopped into pieces for melt index determinations.

Melt flow measurements were carried out in a Slocomb Melt Indexer with a Sargent Thermonitor Model S for temperature control. ASTM procedure D1238-65T was normally followed. In the melt flow experiments at various temperaures, the sample weight and procedure as required for a normal melt index determination were used throughout. During the course of the work it was also found necessary to use a single melt indexer orifice in any one series of experiments in order to improve internal consistency of the results.

Inherent viscosities were measured in tetralin at 130°C. as previously described.[3]

RESULTS

In the first series of experiments, six polymer samples were compression-molded at various temperatures and for varying lengths of time. The change in melt index for five of these samples is shown in Figure 1, the effect of temperature on the sixth sample in Figure 2. In the absence of any shearing effects, all the samples showed a sharp drop in melt index. Only at 315°C. did sample A-1 (Fig. 2) show a subsequent increase to a value higher than the initial melt index.

When samples were extruded, however, the results were quite different. All of the samples exhibited an increase in melt index, the magnitude of
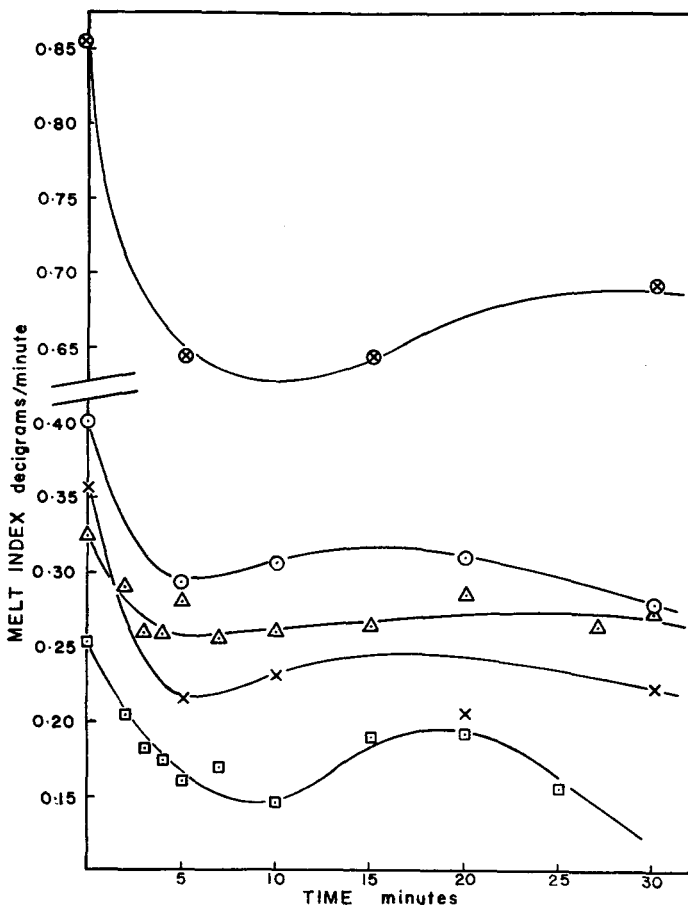

Fig. 1. Effect on melt index of heating various polyethylenes in compression mold: (□) sample B-2, 250°C.; (⊙) sample C-1, 260°C.; (△) sample C-2, 175°C.; (✕) sample C-3, 260°C.; (⊗) sample D-1, 290°C.
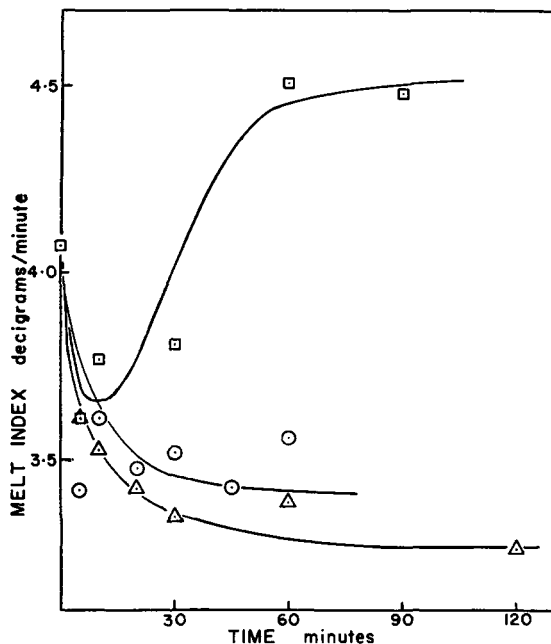
Fig. 2. Effect on melt index of heating sample A-1 in compression mold at various temperatures: (△) 190°C.;   (⊙) 230°C.;   (▫) 315°C.

which depended on extruder rate.   These data are presented in Figure 3. Sample B-2 (Fig. 3a) did show a decrease in melt index but only at the highest extrusion rates.   Since these samples, when received in the laboratory, had already been extruded in the production unit, it is difficult to attribute these melt index changes to improved mixing, as suggested by Heitmiller et al.[1]

Figure 4 is included in order to show the effect of extrusion conditions on the melt index change.   In the experiments shown in Figure 3, the extruder temperatures were set at 175°C., but the front zone normally ran higher than this, depending on the extrusion rate and melt viscosity of the polymer. Using sample B-2 which had been studied in the normal manner, a run was carried out in which the front zone temperature was controlled at 250°C. The results are illustrated in Figure 4a.   Shown as Figure 4b are the melt index values from Figure 3 for sample B-2 plotted against the front zone temperature.   In another experiment, the extruder rate was held constant at 22 rpm and the temperature controlled at various values.   The results for this are shown in Figure 4c.   Evidently temperature and shear rate tend to give different effects.   Low-temperature extrusion increases melt index; increasing rate at constant temperature and increasing temperature at constant rate both decrease melt index.

Further experiments designed to indicate the effect of temperature on melt viscosity in a low shear situation were carried out by measuring melt
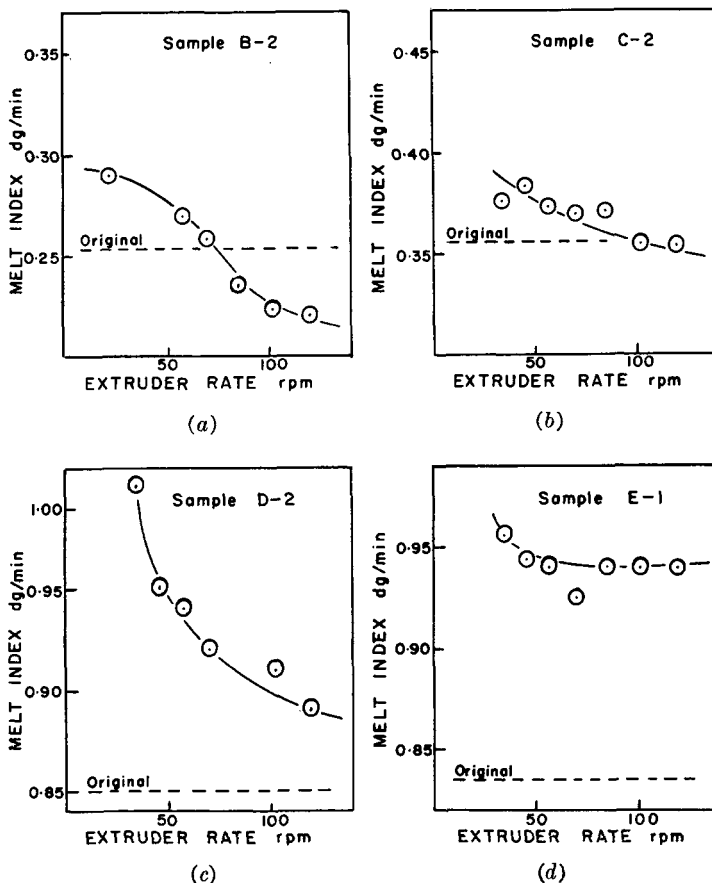
Fig. 3. Effect of extrusion rate on melt index.

flow at various temperatures using the standard melt index procedure. From a simple flow theory, the logarithm of the melt flow rate should be an inverse linear function of absolute temperature.[4,5] The data obtained, presented graphically in Figure 5, clearly indicate that a simple linear relationship is not observed in many cases. For three of the four resins, over the temperature range from about 190 to 235°C., the melt flow rate became virtually independent of temperature. Above 235°C., melt flow rate again increased in the expected manner. Only for sample D-3 did the linear relationship hold over the entire temperature range.

During the course of this work it became evident that re-extrusion and addition of stabilizer could influence the relationship between melt flow rate and temperature. Thus sample B-4 was re-extruded alone, and re-extruded at two different temperatures with 200 ppm of additional stabilizer (2,6 di-*tert*-butyl *p*-cresol). Figure 6 illustrates the results of these experiments. Clearly, the deviation from linearity in the curves is reduced as the polymer is stabilized and re-extruded.

Samples of resins which had been heated in the compression mold for various lengths of time were taken for inherent viscosity determinations. The results are shown in Figure 7. Two of the samples showed a marked decrease in solution viscosity even though the melt viscosity under the same conditions had gone up as shown in Figure 1. The third sample showed no change in solution viscosity.
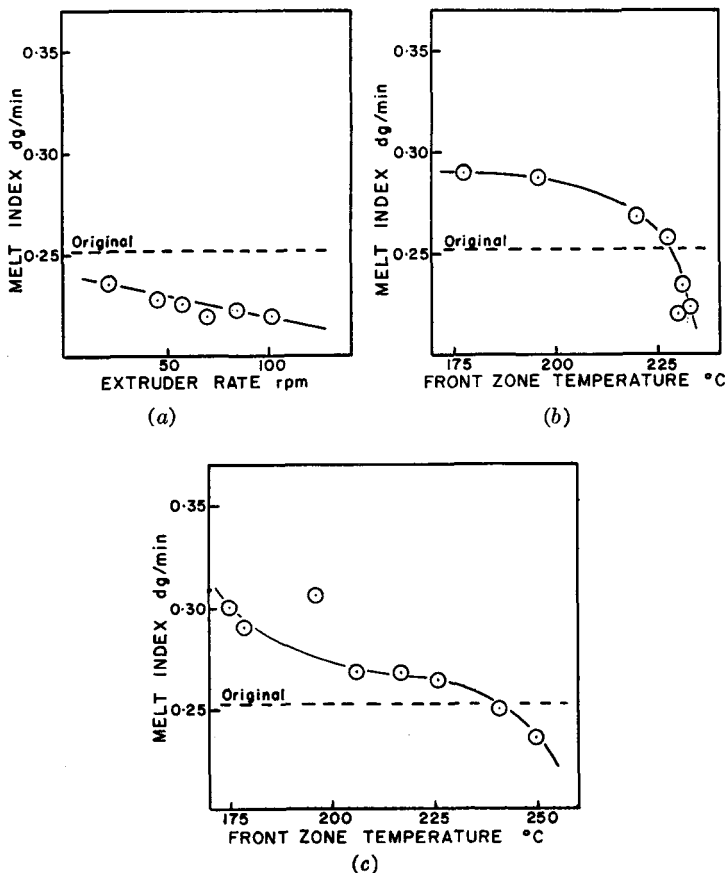

Fig. 4. Effect of extrusion conditions on melt index of sample B-2: (a) effect of extrusion rate at constant front zone temperature of 250°C.; (b) effect of front zone temperature at the various rates indicated in Fig. 3a; (c) effect of front zone temperature at a constant extruder rate of 22 rpm.

On extrusion, the solution viscosity of two samples studied also decreased, particularly at the low extrusion rate. In this case, however, the melt viscosity, as shown in Figure 3, had also decreased at the low rates. Thus during extrusion both melt and solution viscosity point to a decrease in average molecular weight, whereas on compression molding, the two viscosity measurements indicate opposite changes in average molecular weight.
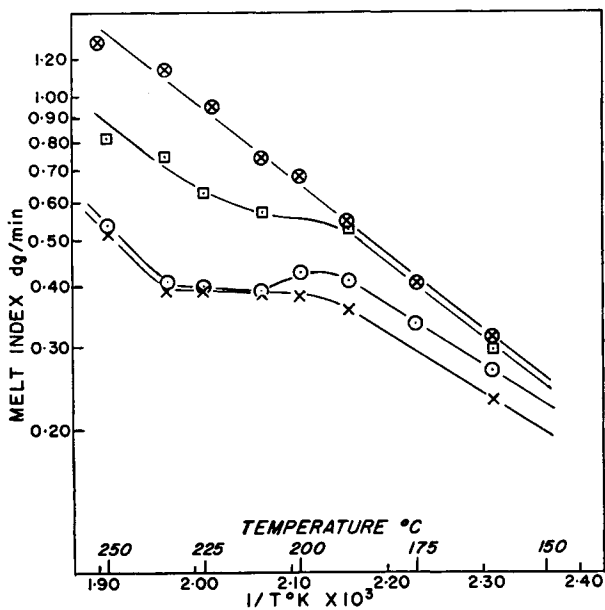
Fig. 5. Melt flow as a function of temperature: (□) sample B-1; (×) sample C-3; (⊙) sample C-4; (⊗) sample D-3.
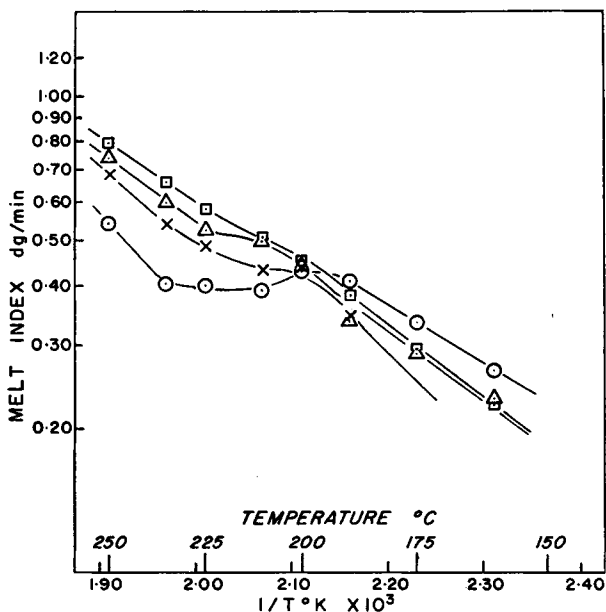

Fig. 6. Effect of additives and re-extrusion on relationship between melt flow and temperature: (⊙) sample C-4 as received; (×) re-extruded at 230°C.; (△) re-extruded with 200 ppm 2,6-di-*tert*-butyl *p*-cresol at 230°C.; (□) Re-extruded with 200 ppm 2,6-di-*tert*-butyl *p*-cresol at 260°C.
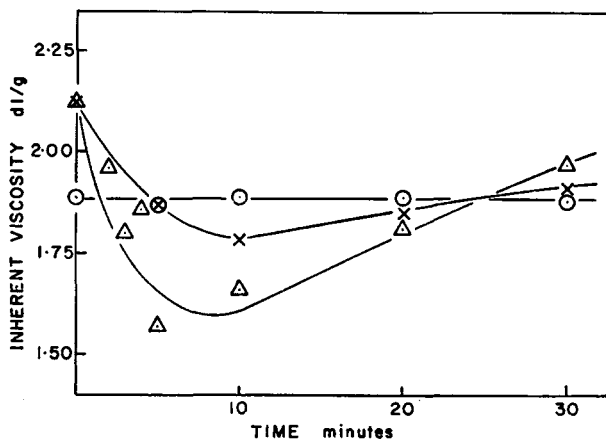
Fig. 7. Effect on inherent viscosity of heating various polyethylenes in compression mold: (⊙) sample C-1; (△) sample C-2; (✕) sample C-3.
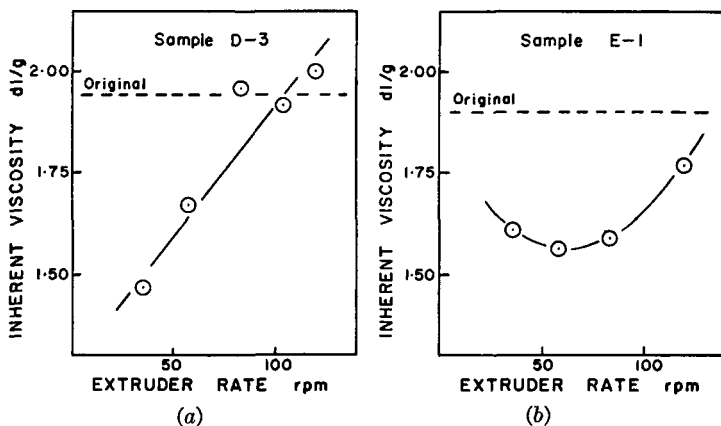

(a)   (b)

Fig. 8. Effect of extrusion rate on inherent viscosity.

DISCUSSION

The results presented above demonstrate the complexity of the processes which occur when linear polyethylene is heated and extruded.   The following hypothesis is an attempt to rationalize these apparently contradictory results.

When ethylene is polymerized, a small number of double bonds are inevitably introduced.   During subsequent drying and extrusion, a certain amount of oxidation generally occurs.   As a result, polyethylene always contains a few potentially reactive sites.   During heating, such sites may undergo reactions that produce free radicals which in turn can then produce either chain scission or crosslinking, depending on conditions.   With little or no shearing action in the melt, crosslinking rather than chain scission appears to be the dominant reaction, thus leading to a higher melt viscosity.

At the same time, the resulting highly branched molecules apparently have a lower solution viscosity than would be anticipated on the basis of simple additivity. Thus the drop in melt index on compression molding and the peculiar relationship between melt flow and temperature can be explained by such a crosslinking reaction.

On the other hand, in an extrusion process, where the molecules are less liable to form crosslinks, chain scission then becomes the dominant reaction. In this manner the average molecular weight decreases, as reflected by both the solution and melt viscosities. Presumably as the extrusion rate increases the polymer is given less and less time to react, hence the viscosity change decreases at the high rates.

To summarize, linear polyethylene apparently contains reactive sites which can lead to both chain scission and crosslinking. The relative importance of these two reactions is determined by the temperature and shear conditions, high shear favoring scission and low or zero shear favoring crosslinking. Additional experiments are under way in this laboratory to clarify these effects further.

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