Shear Modification of Low Density Polyethylene

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Synopsis

A single screw extruder was used to impose different shear histories on a low density polyethylene with broad molecular weight distribution and high molecular weight tail that had very little long chain branching. This polymer exhibits relatively high melt elasticity and the viscoelastic properties of its melt are strongly affected by preshearing. Such changes are accomplished without significant changes in molecular weight distribution or chemical structure. Measured viscous and elastic properties of the melt are different from piston-driven and screw extruder capillary rheometers. Shear modification effects in single screw extruders are enhanced by decreasing melt temperature, increased screw rotation speeds, and higher screw compression ratios. Melt elasticity can be cycled between high and relatively low values, for the particular polymer, by annealing or shearing the polymer melt.

INTRODUCTION

A previous article from this laboratory has described a systematic procedure for rheological characterization of polyethylene by capillary extrusion experiments.[1] This technique has been applied to describe the effects of shearing history on the viscoelastic properties of a linear low density polyethylene sample.[2] This polymer exhibited modest changes in melt properties as a result of preshearing. Such differences, which occurred without any change in molecular weight distribution or polymer constitution, were apparent in measurements made with a piston-driven capillary rheometer. Rheological measurements in a laboratory screw extruder did not show the effects of shear history, however, because the shear working on the screw erased differences in entanglement densities of the various samples fed to the extruder.[2]

This article reports the study of a polyethylene that has a higher initial entanglement density than the linear low density polymer studied earlier. In this case, the effects of shearing history are pronounced and the results of rheological assessments by piston-driven and screw extruder capillary viscometers are shown to be fundamentally different. The effects of preshearing conditions on the extent of shear modification are summarized. The effects observed are consistent with the general scheme of shear modification processes that has been summarized elsewhere.[3]

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EXPERIMENTAL

Low density polyethylene with a melt index of 0.3 dg/min and a nominal density of 0.920 g/cm³ was stabilized before extrusion with 0.2% (w/w) 4,4'-thiobis(3-methyl-6-*tert*-butylphenol) antioxidant.

Melt flow behavior was studied with a fixed plunger speed mechanically driven capillary viscometer—the Instron rheometer[4]—and a laboratory scale 0.5-in. diameter screw extruder.[1] Flat-entry capillary dies of 2.5 mm diameter with length to diameter (L/D) ratios of 4, 8, 12, and 20 were used with the Instron rheometer and dies of 3.2 mm diameter with L/D ratios of 2, 8 and 16 were employed with the laboratory extruder. Instron rheometer shear rates were varied from 4.9 s⁻¹ to 155 s⁻¹ whereas the span of shear rates for the laboratory extruder was from 6 s⁻¹ to 77 s⁻¹. Extrusion temperatures ranged from 150°C to 230°C.

Shear modification experiments were performed in the laboratory screw extruder where the parameters varied were orifice L/D ratio, extrusion temperature, mass flow rate of polymer, number of passes through the extruder, residence time in the machine between the screw tip and the die entrance, and the screw compression ratio. The extrudate swell ratio was obtained by a procedure described earlier.[1] The shear-modified samples were examined with the Instron rheometer to determine the extrudate swell behavior. They were also characterized by size exclusion chromatography with respect to molecular weight and long chain branching distributions. Molecular weight and long chain branching characteristics of this polymer are described in a separate section later in this article.

RESULTS AND DISCUSSION

Flow Curves of LDPE

Figure 1 shows the flow curves (apparent shear stress vs. apparent shear rate) of the polyethylene obtained from the Instron rheometer at 190°C with capillary dies of 2.5 mm diameter and L/D ratios of 4, 8, 12, and 20. For apparent shear rates equal to and smaller than 15.5 s⁻¹, smooth extrudates
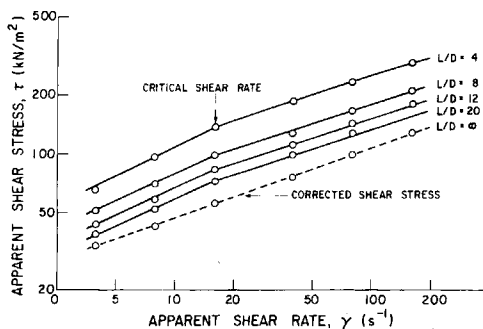

Fig. 1.   Apparent shear stress–apparent shear rate plot for low density polyethylene sample at 190°C. Data were obtained under constant plunger speed conditions with Instron rheometer capillary dies of 2.5 mm diameter. The $L/D = \infty$ plot is after correction of the apparent shear stresses for entrance effects.

were obtained. Above this shear rate, melt fracture set in, and the severity of extrudate distortion increased with increasing shear rate. The flow curves may be fitted with two straight lines, one for smooth extrudates, and one for distorted extrudates, intersecting at the shear rate corresponding to the critical shear rate for the onset of melt fracture for the range of L/D ratios investigated. The apparent flow curve for infinite L/D was obtained by applying Bagley end corrections[5] to the measured flow curves.

By contrast, smooth extrudates were obtained with the laboratory screw extruder at all shear rates up to 77 s^{-1} for extrusion with a capillary die of 3.2 mm diameter and L/D ratios of 2, 8, and 16. Each apparent flow curve could be represented by a single straight line, as shown in Figure 2. The corrected flow curve in Instron rheometry (Fig. 1) represents a higher viscosity than the screw extruder flow curve at low shear rates. The two coincide at a shear rate 100 s^{-1}.

We show below that the polymer molecular weight was not altered significantly by this extrusion. Rheological structures in the polymer appear to have been shear modified in the screw region of the apparatus. The extent of shear modification was greater at faster screw speeds, or higher mass flow rates. This was shown by extrusion at 190°C through a 1.6 mm diameter die of $L/D = 8$, at a screw speed of 5 rpm (mass flow rate = 0.86 g/min) where severe melt fracture was observed. For this condition the shear rate in the capillary was 48 s^{-1}. On the other hand, no melt fracture was observed at 190°C and 50 s^{-1} in the 3.2 mm die with $L/D = 8$. Here the screw speed was 40 rpm (mass flow rate = 7.2 g/min), and the polymer was more extensively sheared in the screw region.

Bagley end correction plots[5] yielded shear rate dependent end corrections for constant plunger speed operation (Instron rheometer). A single-valued end correction was obtained, however, for constant pressure extrusion (screw extruder). This is shown in Figure 3. This difference in end correction
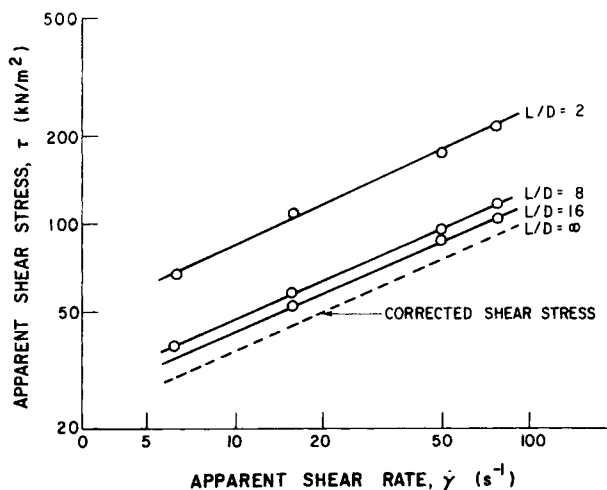

Fig. 2. Apparent shear stress–apparent shear rate plot for low density polyethylene sample at 190°C. Data were obtained under constant pressure conditions with a laboratory screw extruder and 3.2 mm diameter dies.
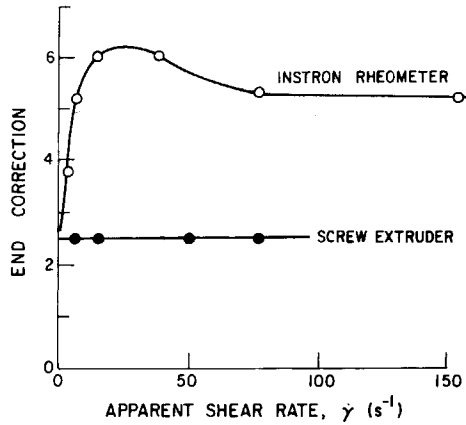
Fig. 3. Dependence of Bagley end corrections on shear rate for constant pressure (●) (screw extruder) and constant plunger speed (○) (Instron rheometer operation).

behavior is probably not due to the different modes of flow in the two capillary instruments.[6] It is believed to reflect differences in the state of chain entanglements of the polymer melt, with a lower entanglement density in the shear-modified polyethylene (screw extrusion) than the unmodified polymer (Instron rheometer). Entrance pressure losses are known to be manifestations of melt elasticity,[7] as are die swell, melt fracture, and normal forces.[8]

Figure 4 shows flow curves of this polymer at different emperatures. These measurements were made with the Instron rheometer with a capillary die of 2.5 mm diameter and $L/D = 8$. The critical shear rate at which melt fracture first occurred increased with increasing temperature, as shown in Table I. However, the corresponding critical shear stress varied much less over this temperature range, although it, too, increased modestly at higher temperatures. The critical shear rate at which extrudate distortion is apparent visually is always higher than that estimated from the intersection of straight line portions of the flow curve. This is understandable since the melt fracture can occur without gross variations in extrudate appearance.[9]
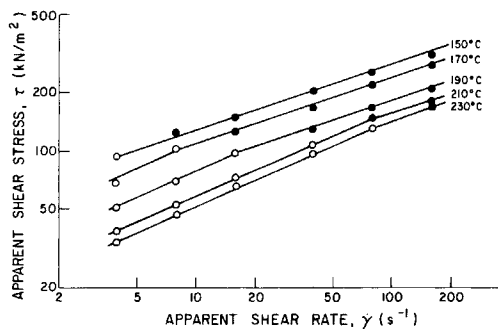

Fig. 4. Apparent shear stress as a function of apparent shear rate at different temperatures. Instron rheometer data for capillary die diameter of 2.5 mm and L/D ratio of 8: (●) melt fracture; (○) smooth extrudate.

TABLE I
Dependence of Critical Conditions for Flow Instability on Temperature of Extrusion for
LDPE Extruded with the Instron Rheometer[a]

Temperature (°C)	150	170	190	210	230
Apparent shear rate at which melt fracture was first observed visually (s^{-1})	7.7	15.5	38.7	77.4	155
Critical apparent shear rate obtained from intersection of flow curves, γ_c (s^{-1})	> 3.8	9.0	17	55	100
Critical apparent shear stress obtained from intersection of flow curves, τ_c (kN/m^2)	> 95	100	100	125	155
Critical apparent melt viscosity, η ($\times 10^{-3}$ P) at onset of melt fracture	—	11.1	5.9	2.3	1.5

[a] 2.5 mm diameter die with $L/D = 8$.

In screw extruder operation melt fracture was not observed with a 3.2 mm die ($L/D = 8$) at any extrusion temperature as low as 160°C and shear rates up to 50 s^{-1}. We interpret this to indicate that the onset of melt fracture was shifted to more extreme extrusion conditions as a consequence of shear-induced reductions in the entanglement density of the polymer before it reached the extrusion orifice.

Table II shows the apparent viscosities of samples of this polyethylene, as measured at 190°C in the Instron rheometer with a 2.5 mm diameter, $L/D = 8$, orifice. As mentioned, the as-received polymer exhibited melt fracture at shear rates greater than 38.7 s^{-1} (Table I). None of the presheared samples showed any flow instability at shear rates up to 155 s^{-1}, however, although the apparent viscosities recorded in Table II do not differ significantly between the as-received and presheared polyethylenes. This is another example of the observation that shear modification may affect melt elasticity without major changes in apparent viscosity.[2,3]

The Instron rheometer end corrections measured with as-received polyethylene increased with increasing shear rates and reached a maximum at

TABLE II
Apparent Melt Viscosity of Untreated and Presheared LDPE Tested with the Instron
Rheometer at 190°C Using Capillary Die of 2.5 mm Diameter and L/D Ratio of 8[a]

Apparent shear rate (s^{-1})	7.7	15.5	38.7
Apparent melt viscosity ($\times 10^{-3}$ P)			
Untreated LDPE (sample A)	8.9	6.4	3.3
Presheared sample D	9.5	6.0	3.4
Presheared sample E	9.9	6.4	3.4
Presheared sample F	9.2	6.1	3.5
Presheared sample H	8.9	6.1	3.4
Presheared sample G	9.8	6.4	3.5
Presheared sample L	8.9	5.7	3.1

[a] Preshearing conditions (3.2 mm diameter die, mass flow rate 7.2 g/min, screw extruder): sample D, 190°C, $L/D = 8$; sample E, 190°C, $L/D = 2$; sample F, 190°C, $L/D = 16$; sample H, 160°C, $L/D = 8$; sample G, 220°C, $L/D = 8$; sample L, 190°C, $L/D = 8$, repeated extrusion eight times.

the onset of flow instability (Fig. 3). Bagley[5] also observed a change in the end correction at the onset of melt fracture.

At all shear rates the end corrections measured in the Instron rheometer are greater than those in the screw extruder, where melt fracture was not observed. This is further evidence for the existence of greater melt elasticity in the samples that were not shear modified in the extruder.

Extrudate Swell Behavior

The extrudate swell ratio B is defined here as the ratio of the diameter of the frozen, unannealed extrudate to the diameter of the die. The swell ratio decreased rapidly with increase in L/D ratio of the capillary die at given apparent shear rates. This is shown in Figure 5 for three different Instron rheometer shear rates at 190°C. For comparison, this figure also includes the L/D dependence of the swell ratio of a linear low density polyethylene (LLDPE) that has been studied earlier.[1] The molecular weight distribution of the LLDPE did not have as pronounced a high molecular weight tail as this LDPE, and it exhibited less variation of melt elasticity with shearing history.

Figure 6 shows the swell ratio as a function of shear rate for Instron and screw extruder measurements on the LDPE sample. The data are reported for extrudates that are not seriously distorted as a result of melt fracture. A decrease in swell ratio with increasing shear rate is observed in screw extruder measurements. This, again, is probably a manifestation of shear-induced disentanglement in the extruder barrel at higher screw speeds. This behavior is somewhat unusual. Polymers that have melts that are less elastic to begin with exhibit swell ratios that increase monotonically with apparent shear rate at a given temperature.[10]
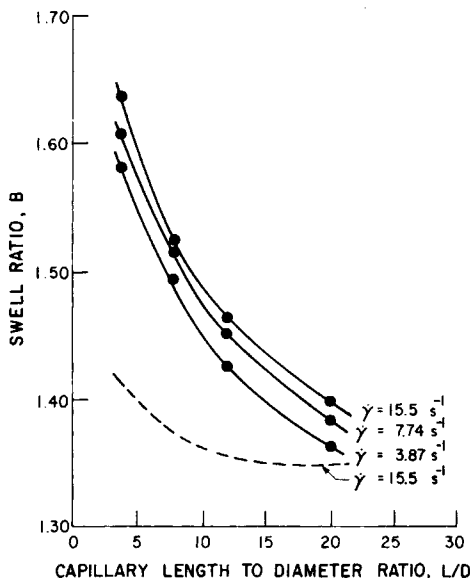

Fig. 5. Low density polyethylene extrudate swell ratio from Instron rheometer at 190°C with a capillary die diameter of 2.5 mm as a function of L/D ratio at fixed apparent shear rates (—), corresponding curve for linear low density polyethylene sample (1).
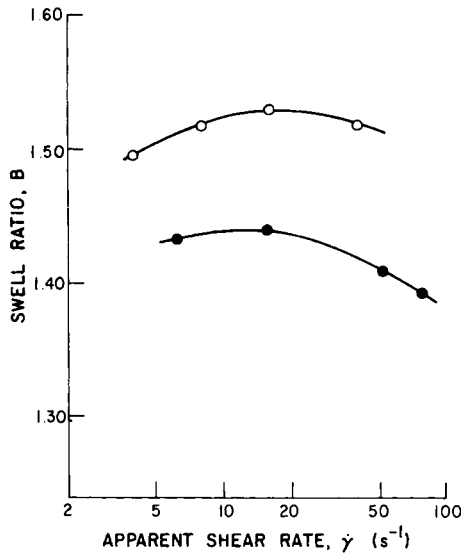
Fig. 6. Swell ratio vs. apparent shear rate for extrudate obtained at 190°C: (○) Instron rheometer capillary die 2.5 mm diameter, L/D ratio of 8; (●) screw extruder, 3.2 mm diameter, L/D ratio of.

The apparent decrease in Instron die swell values shown in Figure 6 occurs in the shear rate region in which melt fracture is first manifested.

Figure 7 shows the dependence of swell ratio on melt temperature at various shear rates. All relations increase with higher temperatures. The screw extruder values are consistently lower than the Instron rheometer data.
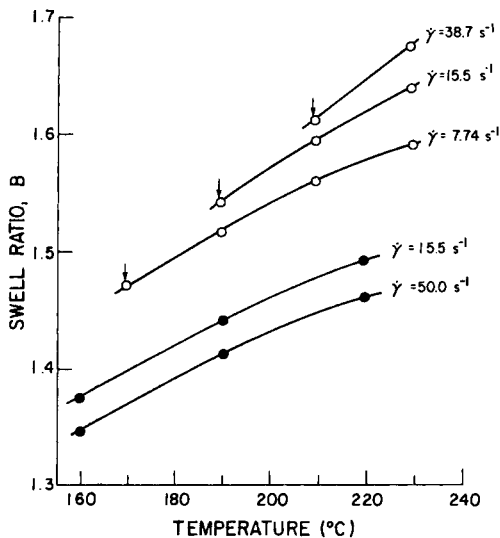

Fig. 7. Dependence of extrudate swell ratio on temperature of extrusion at constant shear rates: (○) Instron rheometer data for LDPE; (●) screw extruder data for LDPE; (↓) indicates beginning of melt fracture.

Data are plotted at given temperatures vs. apparent shear rates in Figure 8. Instron swell ratios increase with increasing temperatures. The highest die swells were measured at 190°C, however, after annealing the polymer melt at this temperature for 18 h in the rheometer barrel. Swell ratios from screw extruder experiments are consistently lower than Instron values at the same shear rate and temperature. Screw extruder swell ratios also increase with increasing experimental temperature, however. All the observations are consistent with a melt characterized by higher entanglement densities at warmer temperatures where segmental mobility is greater. A previous study with a LLDPE sample showed that lower preshearing temperatures enhanced shear modification effects.[2] This parallels the effects depicted in Figure 8, for different screw extrusion temperatures.

In several screw extruder experiments the polymer was annealed in the extruder barrel by stopping the rotation of the screw and leaving the stationary melt hot. When extrusion was restarted, the diameter of the extrudate was observed to decrease with increasing extrusion time until it reached a constant value after extrusion of an amount of polymer corresponding to the mass held up in the residence zone between the screw tip and die entry.

The highest swell ratio measured during screw extrusion of material that had been annealed in the extruder at 190°C was comparable to values obtained from the Instron rheometer for samples annealed in the latter instrument, as described earlier. This is reasonable, since the material annealed in the extruder barrel was located such that it was subsequently extruded without being worked on the screw. The extruder and Instron extrudate swell figures for annealed samples are plotted on line A of Figure 9.
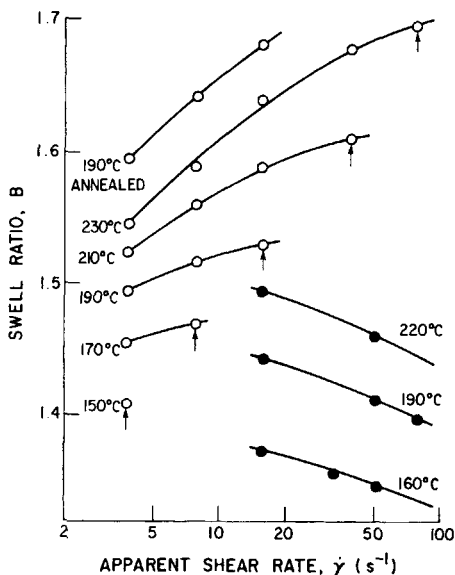

Fig. 8.   Extrudate swell ratio of LDPE vs. apparent shear rate at different temperatures: (○) Instron rheometer 2.5 mm diameter, *L/D* ratio = 8 capillary; (●) screw extruder 3.2 mm diameter *L/D* ratio = 8 capillary; (↑) indicates beginning of melt fracture.
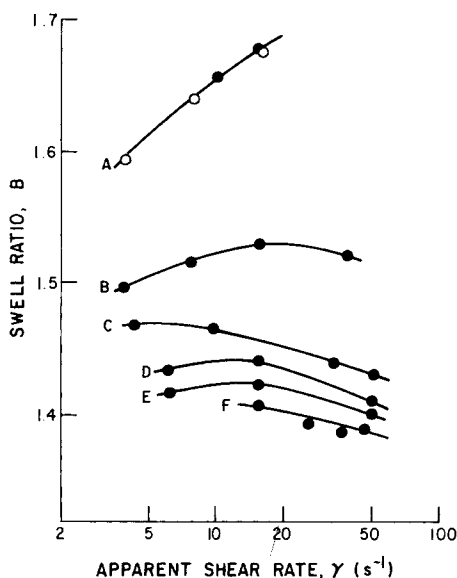
Fig. 9.   Extrudate swell ratio of LDPE vs. apparent shear rate at 190°C for screw extruder capillary die of 3.2 mm diameter, L/D ratio = 8: (A) Annealed samples; (●) screw extruder and (○) Instron rheometer; (B) Instron rheometer data (as in Fig. 6); (C) screw extruder, 3:1 compression ratio screw, 2.5-in. residence zone length; (D) screw extruder, 4:1 compression ratio screw, 4-in. residence zone length; (E) screw extruder, 4:1 compression ratio screw, 2.5-in. residence zone length; (F) screw extruder, 4:1 compression ratio screw, 2.5-in. residence zone length, sample preextruded at 50 s^{-1} before die swell experiment.

The screw compression ratio was found to play a significant role in shear modification. A high compression ratio screw was more effective in the shear disentanglement process and yielded a lower swell ratio. This is shown in Figure 9 curves C and D, for compression ratio 3:1 and 4:1, respectively. At the same mass flow rate, a higher compression ratio screw is effectively giving a higher degree of shearing to the melt.

The effect of annealing on swell ratio was further demonstrated by varying the length of the residence zone between the screw tip and die entrance. This extruder is not equipped with a screen pack or breaker plate, and the space between the screw tip and orifice entrance is a simple conduit. Residence zones with lengths of 2.5, 4, and 7 in. were used with the 0.5-in. diameter extruder. Curves D and E of Figure 9 summarize screw extruder swell ratio data for a 4:1 compression ratio screw feeding polymer into a medium length and short residence zone, respectively. Operation with a larger residence zone produces a melt with higher die swell, presumably because the polymer that has been sheared on the screw can reentangle to some extent in the region between the screw tip and die if its residence time there is long enough.

Repeated passes through the extruder also reduced the melt elasticity of this polymer. This is shown in curve F of Figure 9. In this experiment a sample extruded at a shear rate of 50 s^{-1} was reextruded over a range of shear rates from 15 s^{-1} to 50 s^{-1}. A similar trend was observed earlier for an LLDPE sample.[2]

The effects of repeated extrusion are shown also in Instron rheometer measurements on samples that have been given various shearing histories in the screw extruder. These are shown in Figure 10, which also gives die swell measured on the screw extruder under comparable conditions. The extruder swell ratios are consistently lower than Instron rheometer figures because the polymer melt is allowed to anneal and reentangle to some extent in the reservoir of the latter instrument.

Molecular Weight and Branching Distribution

Molecular weights and long chain branching were measured by size exclusion chromatography in trichlorobenzene at 145°C. The procedures for eliminating aggregates and determining long chain branch frequencies are discussed elsewhere.[10,11]

Parameters of the molecular weight distribution of this polymer are summarized in Table III, where data are given for samples with various, specified shear histories. It can be seen that the molecular weight distribution is not affected to any significant extent, even for samples that have been extruded several times (compare entries for A and J).

Sample L, which was extruded eight times, evidently suffered some degradation of high molecular weight species. The same is true to a lesser extent of sample K, which was extruded three times, and sample G, after extrusion at 220°C.

This polyethylene did not have a high incidence of long chain branches initially. This is shown by curve A in Figure 11, in which long chain branching is plotted as a function of molecular weight.[11] Sample J apparently suffered some increase in long chain branching at low molecular weights,
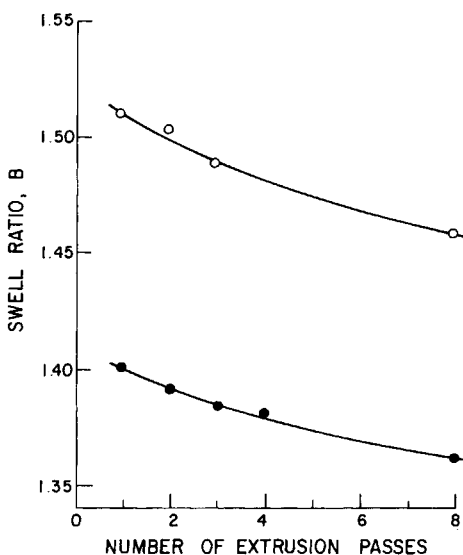

Fig. 10. Dependence of extrudate swell ratio on number of passes through extruder. Extrusion temperature 190°C, 4:1 compression ratio screw, capillary die of 3.2 mm diameter, and L/D ratio of 8: (●) swell ratio directly measured at 5 s⁻¹ on extrudate from screw extruder; (○) Instron rheometer swell ratio at 50 s⁻¹ for treated samples, 2.5 mm die, L/D = 8.

TABLE III
Molecular Weight as a Function of Extrusion History

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	SD of no. distribution S_n [13]	SD of wt distribution S_w [13]	Skewness of no. distribution [skew (N)] [13]	Skewness of wt. distribution [skew (W)] [13]
A	33,000	164,000	5,682,000	65,000	951,000	106	288
B	34,500	169,000	5,573,000	66,000	971,000	107	293
C	30,000	163,000	5,100,000	63,000	949,000	104	286
D	32,000	165,000	5,500,000	65,000	953,000	106	289
E	33,000	166,500	5,700,000	66,000	961,000	106	290
F	30,000	160,000	5,000,000	60,000	931,000	102	278
G	30,000	157,500	4,750,000	61,000	925,000	102	273
H	31,000	166,000	5,800,000	63,500	958,000	103	290
I	32,000	165,000	5,600,000	66,000	950,000	105	288
J	30,000	166,000	5,700,000	61,000	960,000	105	290
K	30,000	162,000	5,150,000	60,500	947,000	105	281
L	21,000	148,000	1,600,000	43,500	541,000	76	183

Extrusion history[a]

Sample	Temp (°C)	Shear rate (s^{-1})	Orifice L/D	Residence zone length (in.)
A	(as received granules)			
B	(annealed 18 h, 190°C in Instron rheometer)			
C	190	6	8	4
D	190	50	8	4
E	190	50	2	4
F	190	50	16	4
G	220	50	8	4
H	160	50	8	4
I	190	50	8	2.5
J	190	50	8	2.5 Extruded 2 times
K	190	50	8	2.5 Extruded 3 times
L	190	50	8	2.5 Extruded 8 times

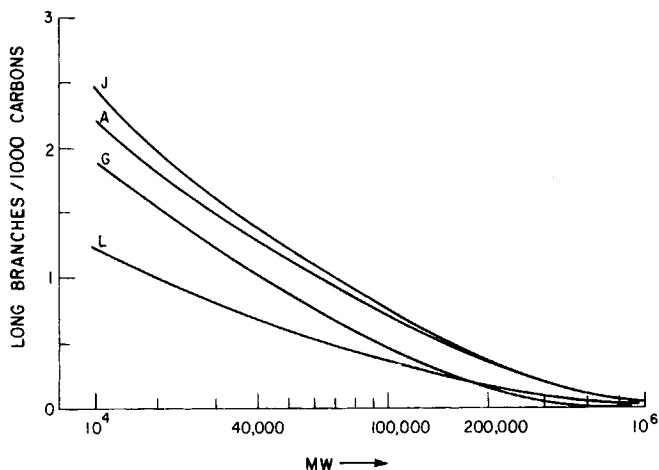[a] All samples were extruded with 4:1 compression ratio screw.

Fig. 11. Long chain branching as a function of molecular weight. (A) LDPE as received; (J) extruded twice at 190°C (see Table III); (L) extruded eight times at 190°C (Table III); (G) extruded at 220°C (Table III).

after two extrusions at 190°C. As shown in Table III, however, there was no detectable difference in molecular weight between samples A and J, and the significance and interpretation of the observed differences in long chain branching is not clear.

Samples G and L, which were processed under more severe conditions, underwent losses of high molecular weight species and long branching, as shown in Table III and Figure 11, respectively.

Most of the samples, however, suffered no change in molecular weight or long chain branching along with the observed larger variations in melt elasticity.

DISCUSSION

The viscoelastic properties of this polyethylene melt are evidently susceptible to shear working. As a consequence, the melt elasticity and, to a lesser extent the apparent melt viscosity, can be modified without significant changes in the molecular weight distribution or chemical structure of the polymer. The changes observed can be rationalized in terms of shear-induced changes in entanglement density.[3]

We believe this polymer can achieve a relatively wide range of entanglement densities because its equilibrium, high entropy state is highly entangled. It is suggested that this reflects the detailed nature of the molecular weight distribution, and particularly the existence of high molecular weight species ($M_z > 5,000,000$) that carry few or no long branches. The fact that this is a low density polyethylene with short branches is incidental to the behavior reported here, in our opinion.

Viscous and elastic melt property measurements on polymers of this type are not independent of the measuring system, as shown here by the different results from piston-driven and screw extruder capillary rheometers. Similar results have been reported for a linear low density polyethylene.[2] Polymers

that are less entangled will exhibit less or no variation in responses to different characterization techniques.

Shear modification effects in single screw extruders are seen to be enhanced by decreasing the melt temperature, increasing the screw rotation speed, and increasing the compression ratio of the screw. From this and earlier work[1,2] it appears likely that the major portion of shear modification occurs when the polymer is worked along the screw. Shearing through the orifice seems to provide a smaller effect. A more fully entangled state is recovered when the melt is allowed to stand, and the elasticity observed can be influenced by the residence time of the polymer between the screw and orifice entrance.

References

1. J. W. Teh, A. Rudin, and H. P. Schreiber, *Plast. Rubber Processing Appl. (London)*, **4**, 149 (1984).
2. J. W. Teh, A. Rudin, and H. P. Schreiber, *Plast. Rubber Processing Appl. (London)*, **4**, 1157 (1984).
3. A. Rudin and H. P. Schreiber, *Polym. Eng. Sci.*, **23**, 422 (1983).
4. E. H. Merz and R. E. Colwell, *ASTM Bull.*, (232), 63 (1958).
5. E. B. Bagley, *J. Appl. Phys.*, **28**, 624 (1957).
6. A. Rudin and R. J. Chang, *J. Appl. Polym. Sci.*, **22**, 781 (1978).
7. W. Phillipoff and F. H. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
8. E. B. Bagley and H. P. Schreiber, in *Rheology*, F. R. Eirich, Ed., Academic, New York, 1969, Vol. 5.
9. E. B. Bagley and H. P. Schreiber, *Trans. Soc. Rheol.*, **5**, 341 (1961).
10. D. L. T. Beynon and B. S. Glyde, *Br. Plast.*, **33**, 414 (1960).
11. V. Grinshpun, K. F. O'Driscoll, and A Rudin, *Am. Chem. Soc., Div. Org. Coatings Appl., Polym. Sci. Prepr.*, **48**(1), 744 (1983).
12. V. Grinshpun, K. F. O'Driscoll, and A. Rudin.
13. A. Rudin, J. Chem. Ed., **46**, 595 (1969).