Influence of Long Chain Branching on Extrudate Swell of Low-Density Polyethylenes

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Synopsis

An experimental study of extrudate swell has been carried out, involving five low-density polyethylene (LDPE) samples of approximately the same molecular size but of different frequencies of long-chain branching (LCB). The results show that the samples with higher frequencies of LCB exhibit a tendency to swell more than samples of lower frequency. This tendency is more pronounced for short L/D dies and high shear rates. It seems possible that LDPE samples of varying LCB frequencies can be differentiated by determining the swelling ratio (d/D) with orifice dies $(L/D \simeq 0)$ at high throughput rates.

INTRODUCTION

Extrudate swell is a melt flow property that is important in the determination of processability of polymeric materials. It is known to be influenced by molecular structure parameters such as molecular weight, molecular weight distribution (MWD), and the frequency of long-chain branching (LCB). For polystyrenes most authors agree[1-3] that the extrudate swell increases with molecular weight $(\overline{M}_w)$, and MWD. For high-density polyethylenes (HDPE) the same trend has been observed,[4] while Mendelson and Finger[5] and Shroff and Shida[6] reported the converse. Rheological studies with low-density polyethylenes proved that, among other factors, the frequency of long-chain branching is of great importance. While Mendelson and Finger[7] reported that as LCB increases extrudate swell decreases, most recent investigations[8-10] show that the opposite is true, that is, the ratio of extrudate diameter to die diameter increases, for the same conditions, as the LCB increases. Much of the confusion regarding the influence of LCB is due to the way the various comparisons are made, i.e., whether the comparisons are made at similar molecular weight levels, melt index (MI) values, or molecular sizes. These points are discussed clearly by Wild et al.[8] The results obtained by these authors[8] suggest that extrudate swell is a molecular-size-dependent property and independent of intermolecular entanglement effects. Consequently, measurement of elastic properties might provide a means of determining relative frequencies of LCB for commercial resins. Pedersen and Ram[11] show that the elastic properties of branched polymers, including extrudate swell, can be predicted by taking into account the unperturbed mean-square radii of gyration rather than molecular weight distributions.

The objective of the present paper is to present some new results on the influence of LCB and to show how extrudate swell measurements might be used to differentiate low-density polyethylenes of varying LCB.

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TABLE I
Summary of High Pressure LDPE Properties[a]

Sample	Density	MI	$\overline{M}_n$ $\times 10^{-3}$	$\overline{M}_w$ $\times 10^{-3}$	$\overline{M}_z$ $\times 10^{-3}$	$\overline{M}_{z+1}$ $\times 10^{-3}$	$\overline{\lambda}_{LCB}$ (branches per 1000 C atoms)
A	0.9232	2.24	26.3	110.0	320.3	623.9	1.6
B	0.923	2.10	16.6	83.9	—	—	1.748
C	0.9186	2.04	21.3	201.6	1258.0	3423.0	2.5
D	0.9210	2.51	22.5	143.1	561.0	1193.0	3.4
E	0.919	1.80	15.6	243.1	—	—	4.523

[a] All five samples are approximately the same molecular size with $g\overline{M}_w = (5.4 \pm 0.5) \times 10^4$, where g is the ratio of mean square radii of gyration for branched (LCB) and linear chains of the same number of repeat units.

TABLE II
Experimental Conditions

Variable	Range
Temperature	180°C
Die diameter (D)	1.334 mm
Die length (L)	0–33.03 mm
Shear rate ($\dot{\gamma}$)	2.69–739.0 s^{-1}

TABLE III
Power-Law Parameters

Sample	Consistency index m (Pa·s^n)	Power-law index n
A	0.7139×10^4	0.45
B	0.6354×10^4	0.49
C	0.7288×10^4	0.38
D	0.7389×10^4	0.42
E	0.3500×10^4	0.703

EXPERIMENTAL

Five commercial high pressure LDPE samples of approximately the same molecular size were used in this study, with frequency of LCB, $\overline{\lambda}_{LCB}$ (branches/ 1000 C atoms) varying from 1.6 to 4.526. The molecular weights and LCB frequencies were determined by GPC (with TCB as solvent at 140°C, calibration by carbon-13 NMR for branching distributions).[12] The results, which are summarized in Table I, were kindly provided to the authors by Dr. G. N. Foster, Union Carbide Corporation, Bound Brook, N.J.

An Instron Capillary Rheometer, Model 3211, was used to study the melt flow rheology of the LDPE samples. A series of experiments with dies of varying length to diameter ratios (L/D) was performed at one temperature, 180°C. The shear rates and shear stresses were corrected using the Rabinowitsch and Bagley methods.[13] Extrudate diameters were determined on frozen, unannealed polymer rods by a micrometer. The diameters were corrected for the density variation with temperature, $d/d_0 = (\rho_0/\rho)^{1/3}$. A summary of the experimental conditions is given in Table II.
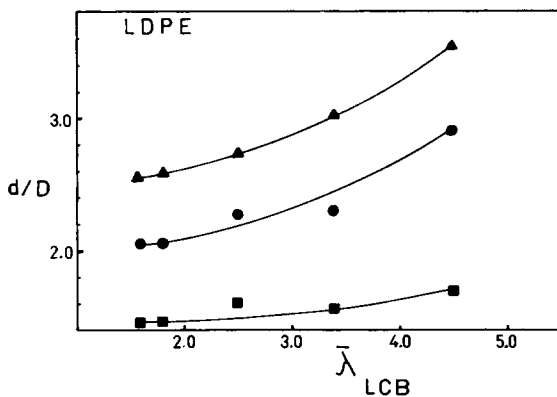
Fig. 1. Extrudate swell as a function of the frequency $\bar{\lambda}_{LCB}$ of LCB. $T = 180°C$; L/D, $\dot{\gamma}$ (s^{-1}): (▲) 0, 600; (●) 2.99, 600; (■) 24.76, 200.

RESULTS AND DISCUSSION

All five samples investigated obeyed the power-law relation between shear stress and shear rate

$$\tau = m\dot{\gamma}^n$$

The consistency index m and the power-law index n are given in Table III. We note that three of the samples (A, C, D) have very similar values of m and n respectively. Although these samples have different molecular weights, MWD, and LCB, they are virtually indistinguishable in their shear flow behavior.

Extrudate swell results from three different L/D dies are shown in Figure 1. As the frequency of LCB increases, the swelling ratio d(extrudate)/D(die) increases. This trend is only slightly noticeable with the long die (shear rate $\dot{\gamma} = 200$ s^{-1}) data, but very pronounced with the orifice die ($L/D \simeq 0$). It is interesting to compare the results for samples C and D. While C has a higher molecular weight and broader MWD (therefore, a tendency to swell more), it has, however, a smaller LCB frequency (therefore, a tendency to swell less) than sample D. The two samples are virtually indistinguishable with $L/D = 24.76$ ($\dot{\gamma} = 200$ s^{-1}) and $L/D = 2.99$ ($\dot{\gamma} = 600$ s^{-1}), while noticeably different with $L/D \simeq 0$ ($\dot{\gamma} = 600$ s^{-1}). An explanation can be given for this type of behavior by as-
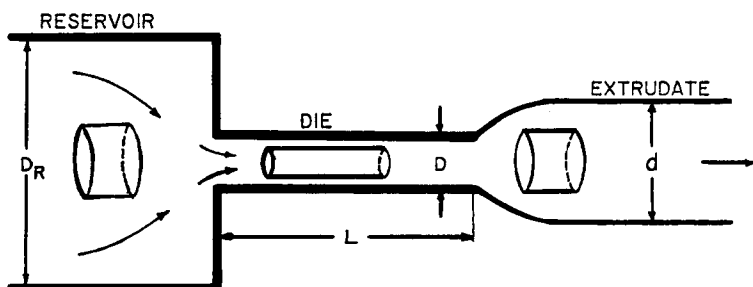

Fig. 2. Schematic representation of the sequence of deformations of a material element as it enters, travels through, and emerges from a die.

suming that extrude swelling is mainly due to two mechanisms,[14] namely: memory of entrance (i.e., an imaginary fluid element in the shape of a cylinder tries upon emerging from a die to regain its original shape as shown in Fig. 2) and elastic recovery (release of normal stresses). When the tube is sufficiently long, the memory of entrance fades completely. Our results suggest that in the case of branched LDPE the samples seem to be more elastic because of enhanced molecular interactions when the frequency of LCB is large. However, when the transit time through a die is long (large L/D, small λ_{LCB}), these interactions are significantly reduced (disentanglement?). Thus, in the case of long transit times it would be mainly the molecular size and the distribution molecular sizes that determine the amount of swelling. Therefore, it is better to state that melt elasticity (memory plus normal stresses), rather than swelling, is increased as the frequency of LCB increases. The amount of swelling depends on combination of molecular weight, MWD, and LCB effects, the latter being important at shorter transit times.

CONCLUSION

From the present study, it seems possible to differentiate samples of high pressure LDPE having approximately the same molecular size but varying degrees of LCB. The larger the degree of LCB, the larger the extrudate swell. We recommend, however, that die swell measurements be made with a very short die (preferably with an orifice die) and at high shear rate values in order to augment the elasticity of the melts and thus make the distinction possible.

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