Influence of Shearing History on the Rheological Properties and Processability of Branched Polymers. V. Effect of Molecular Structural Parameters on Die Swell of Low-Density Polyethylenes

INTRODUCTION

Low-density polyethylene (LDPE) is a typical long-chain branched polymer. Its die swell is known to be a good index predicting the optical properties of blown films or extrusion processability,[1,2] and many researchers have investigated the effects of the molecular structural parameters such as molecular weight and long-chain branching frequency λ on the die swell.[3–5] According to recent studies,[6,7] however, the viscoelastic properties of LDPE is dependent not only on the molecular structural parameters but also on the shearing histories of the materials. For example, the melt viscosity and elasticity of LDPEs are gradually reduced by continuous shearing such as extrusion processing or Brabender shearing and finally reach certain steady values, though no variation takes place in their molecular structural parameters during the shear processing (shear treatment). In addition, melt viscosity and elasticity of the sheared materials spontaneously return to the values they had before shearing by dissolving them in a good solvent and subsequently removing the solvent under reduced pressure (solvent treatment). These experimental results clearly show that it is indispensable to clarify the shearing histories of the materials when we investigate the rheological properties of LDPE.[8] Yet in most studies on the die swell of LDPE carried out in the past, the shearing histories of the materials were not taken into consideration.

The object of this note is to investigate the relationships between the molecular structural parameters and the swell ratios of LDPEs of which shearing histories are identified.

EXPERIMENTAL

Ten LDPEs were used in this study. They were synthesized with an autoclave reactor and classified into the three families, A, B, and C, according to the polymerization conditions.[7] The molecular structural parameters such as weight-average molecular weight M_w, molecular weight distribution MWD, and the long-chain branching frequency λ were determined by the combined use of gel permeation chromatogram and intrinsic viscosity data. The details of measurements were described elsewhere.[8] Table I shows the characteristics of LDPEs: melt flow index (MI), density, M_w, M_w/M_n, and λ. As can be seen from the table, three resins of the B family are about the same in their M_w and MWD (M_w/M_n) but differ in their λ. On the contrary, samples A-0 and B-3 are about the same in their λ but differ in their M_w and MWD.

The materials of which shearing histories were well characterized were prepared in the same way as described in a previous communication.[7] Briefly, full-sheared materials were obtained by shearing LDPE pellets at 190°C for 150 min with a Brabender plasticorder (hereafter we will call the LDPE pellets untreated materials). Solvent-treated materials were obtained by dissolving the untreated LDPEs in hot xylene and subsequently removing the solvent with a vacuum pump at 160°C. No variation in the molecular structural parameters took place during the shear and solvent treatments.

The swell ratios were measured with a melt flow indexer at 190°C at an applied load of 2160 g. The details of the measurements were described elsewhere.[7]

RESULTS AND DISCUSSION

Figure 1 shows the plots of the swell ratios versus the long-chain branching frequency λ for the solvent-treated materials. First, let us investigate the effects of long-chain branching on the swell ratios of the solvent-treated materials. The swell ratios of three resins of the B family, designated by square symbols, decrease as λ increases. As mentioned above, those resins are about the same in their M_w and MWD, so we can say that an increase in λ reduces the swell ratios of the solvent-treated materials. This finding is in good agreement with that of Mendelson and Finger,[9] who in-

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TABLE I
Characteristics of the Materials

Sample No.	MI	Density	$M_w \times 10^{-5}$	$\lambda \times 10^4$	M_w/M_n
A-0	0.6	0.919	5.31	6.9	17.0
A-1	1.1	0.917	5.99	13.8	22.7
A-2	3.3	0.916	4.08	11.0	25.8
A-3	8.1	0.914	3.35	12.2	27.7
A-4	22.6	0.915	2.73	14.3	20.5
B-1	3.1	0.924	1.57	3.3	11.5
B-2	7.8	0.924	1.35	4.2	9.4
B-3	23.0	0.924	1.30	6.0	11.5
C-1	4.5	0.928	0.98	1.7	8.2
C-2	24.0	0.928	0.67	2.1	7.4

vestigated the relationship between melt elasticity and λ using experimentally synthesized LDPEs with the same M_w and MWD. On the other hand, the die swell behavior of the A and C families also shows the same tendency as that of the B family. But these resins are not the same in their M_w and MWD; so, on the basis of these experimental data, we cannot explain how long-chain branching influences the swell ratios.

Next, let us investigate the effects of M_w and MWD on the swell ratios of the solvent-treated materials. This object is readily achieved by comparing the swell ratio of sample A-0 with that of B-3 because these samples are about the same in their λ. The swell ratio of sample A-0 with a M_w of 5.31×10^5 and a M_w/M_n of 17.0 is 1.90, and that of sample B-3 with a M_w of 1.30×10^5 and a M_w/M_n of 11.5 is 1.44. This clearly shows that the swell ratios increase with increase in M_w and MWD. But it is not clear which one, M_w or MWD, strongly governs the die swell of LDPE.

In conclusion, we can say that the swell ratios of the solvent-treated materials increase with increase in M_w and MWD but decrease with increase in λ. By the way, classifying the swell ratios on the basis of the MI range, i.e., 3–5, 7–8, 22–24, the swell ratios increase with increase in λ as shown by the solid lines in Figure 1. This finding seems to be in conflict with the conclusion already mentioned. But if we pay attention to the fact that when comparisons are made at constant MI it is always observed that M_w and MWD are increasing with increase in λ (see Table I), the conflict is readily solved. That

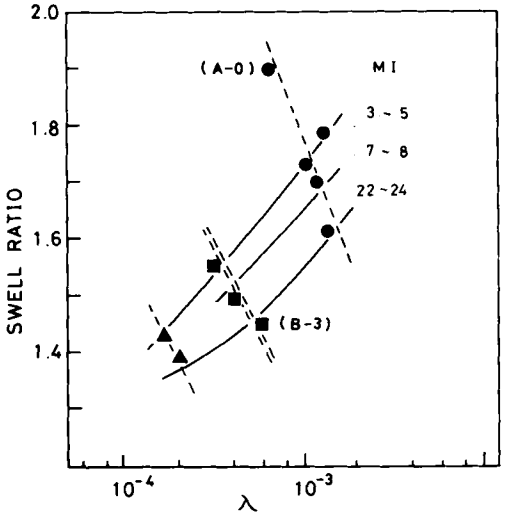

Fig. 1. Relationship between long-chain branching frequency and swell ratios of solvent-treated materials: circles, squares, and triangles designate resins of the A, B, and C family, respectively.

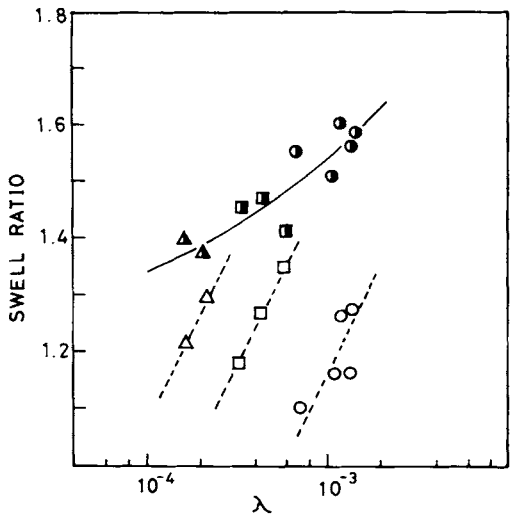

Fig. 2. Relationship between long-chain branching frequency and swell ratios of untreated and full sheared materials. Symbols have the same meaning as in Fig. 1.

is, the effect of M_w and MWD on the swell ratios is stronger than that of λ, and then the swell ratios seemingly increase with increase in λ. The same finding was obtained by Wild et al.,[3] though their materials were not solvent treated.

Figure 2 shows the relationships between the swell ratios and λ for the untreated and the full-sheared materials. In this figure, semifilled symbols refer to the untreated materials and open ones to full-sheared ones. We can see the effects of the shearing histories on the die swell behavior. The die swell behavior of the untreated materials, which are sheared to some extent by the extruder in finishing process, slightly differs from that of the solvent-treated ones. Namely, the swell ratios increase with increase in λ irrespective of MI, as shown by a solid line. On the other hand, the die swell behavior of the full-sheared materials is remarkably different from that of the solvent-treated ones. For example, as shown by the dashed lines in Figure 1, the swell ratios of the solvent-treated materials decrease with increase in λ, but those of the full-sheared ones clearly increase with increase in λ as shown by the dashed lines in Figure 2. In a previous communication,[7] the author explained the cause of the viscoelastic variation induced by the shear processing in terms of a change in the size of the rheological flow units. The change in the size of the flow units probably affects the die swell behavior, and then the relationship between the swell ratios and λ varies corresponding to the shearing histories of the materials.

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