Influence of Shearing History on the Rheological Properties and Processability of Branched Polymers. II. Optical Properties of Low-Density Polyethylene Blown Films

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Synopsis

An investigation was performed to determine how optical properties of LDPE blown films changed when the material was subjected to extrusion shearing. In this study, shearing histories were given to the materials by designed extrusion shearing. Recognizable variations take place in haze and gloss of the blown film during the extrusion shearing. Such variations were expressed as a function of the processing index (PI), which was introduced in a preceding paper as a measure of the memory effect of shearing histories of LDPE. This means that the variations originate in a certain change in the cohesive state of the polymer molecules attributable to the shearing.

INTRODUCTION

When low-density polyethylene (LDPE) melts are subjected to a shearing force, recognizable changes occur in their melt viscosities and elastic properties. According to studies[1–5] on such phenomena, the melt viscosity, die swell, and surface roughness of the extrudate are reduced by shearing the material in the molten state such as extruding or Brabender shearing, but we can make the reduced viscosity and elastic properties go back to their original values by means of holding the processed material for several hours in the molten state (this operation is called heat treatment) or dissolving it in a good solvent and subsequently removing the solvent by evaporation under hot nitrogen atmosphere or reduced pressure (the solvent treatment).

These experimental results demonstrate that LDPE has the unique character of memorizing shearing histories (the effect will be called "memory effect of shearing histories" from now) and also suggest that the development of such character originates in a certain change in the cohesive state of the polymer molecules rather than a structural change of the material due to the shear processing. We have revealed in the preceding paper[5] that such reversible change in the viscoelastic properties of LDPE is strongly dependent upon various molecular parameters: the long-chain branching frequency (number of LCB per weight-average molecular weight), melt index (MI) and shape of the molecular weight distribution (MWD), and/or weight-average molecular weight (M_w). And an index, named processing index, was introduced[5] as a characteristic parameter which indicates a measure of the memory effect of the shearing histories. This peculiar nature of LDPE is possibly reflected in its processability and end-use properties[1,3–4] because most of the products of LDPE are produced by means

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of melt extrusion during which the material is subjected to shearing. In this sense the new characteristic parameter PI is also expected to be useful as a guide of kneading efficiency of the extruder and particularly for predicting the effect of extrusion shearing on the end-use properties of LDPE.

The subject of this paper is to investigate the effect of extrusion shearing on the optical properties of the blown films of LDPE, taking PI as a characteristic parameter of the material.

EXPERIMENTAL

Six commercially available LDPEs were used in this study. Shearing histories were given to the materials by means of passing the materials five times through a 65-mm extruder with a polyethylene-type screw of L/D ratio of 24, to which a pelletizing equipment was attached. Each time the material was extruded, it was pelletized under water for easy handling. Two thousand ppm of the antioxidant 4,4′-thiobis(6-*ter*-butyl-*m*-cresol) was added to the materials in order to prevent thermal oxidation prior to the first extrusion running. The detailed extrusion conditions are shown in Table I.

Also shown in Table I are melt index, density, and processing index (PI) of the fresh materials having no shearing histories (they have undergone some shearing histories during the finishing process for commercialization). Melt index and density are measured according to ASTM D 1238-73, procedure A and D 1505-63T, respectively.

Here, let us give an outline of the PI. As described in the previous paper,[5] the die swell of the extrudate decreases with increase in the time of the shearing, and it finally attains equilibrium S_e after the shearing has been applied to the material for a certain time. Such an equilibrium value depends on the material characteristics but not on the shearing condition. That is, the S_e is the intrinsic value of the material. Such reduction of die swell originates in a certain change in the cohesive state of the polymer molecules, and the sheared material is considered to be in a metastable state.[5] The movement from a metastable state to the stable state is voluntarily achieved by dissolving the sheared material in a good solvent (solvent treatment) or by holding it in the molten state for several hours (heat treatment).[5] Accompanied by the transition of such a material state, the die swell changes from the S_e to S_r, the swell ratio of the material in the stable state. The PI is defined as the ratio of the S_e to S_r, S_e/S_r (where $S_e \leqq S_r$). As can be seen from the definition of the PI, when the PI is unity, the viscoelastic

TABLE I
Characteristics of Fresh Materials and Extrusion Conditions

Sample	Melt index MI	Density	Processing index PI	Temp., °C					Screw speed, rpm
				C-1	C-2	C-3	Head	Die	
A	0.55	0.921	0.89	125	134	151	158	157	50
B	0.56	0.919	0.71	125	134	155	156	157	50
C	1.37	0.924	0.90	124	133	146	157	156	50
D	1.96	0.921	0.92	122	131	146	156	155	50
E	2.97	0.924	0.79	123	130	145	155	155	50
F	7.96	0.924	0.88	120	130	144	154	155	50

properties of the material are independent of the shear processing; but as the PI becomes smaller than unity, the material becomes sensitive to the shearing. For measurement and detailed description of the PI, the preceding paper[5] should be referred to.

The preparations of all the blown films were carried out with a 65-mm extruder having a polyethylene-type screw of L/D ratio 26 and a screen combination of 80, 100, and 80 mesh and a 75-mm spider die under the following extrusion conditions: extrusion temperatures of 130°C in the No. 1 cylinder zone, 140°C in the No. 2 cylinder zone, and 150°C in the No. 3 cylinder zone, head and die, and screw speed is 50 rpm; and blow-up ratios 2.0. All the blown films obtained were 40 μm in thickness. The haze and the gloss were measured according to ASTM D 1003-61 and D 2457-70, respectively.

The die swell was measured at 190°C with an applied load of 2160 g, with the melt indexer designed according to the specification of ASTM D 1238-73, procedure A. In this measurement the molten extrudates were dropped into aqueous solution of ethanol of the same density as that of the extrudate in order to lessen the effect of gravity on the swelling ratio. Here, the swelling ratio is defined as the ratio of the diameter of the extrudate to that of the capillary. MI and the swelling ratio of the fresh materials and of the materials extruded for the fifth time, and haze and gloss of the blown films made from them and the relative haze and relative gloss are shown in Table II. The relative haze and relative gloss are defined as the ratio of the haze and the gloss of the fresh material to those of the material extruded for the fifth time.

RESULTS AND DISCUSSIONS

As can be seen from Table II, the haze of the blown film made from the material extruded for the fifth time is low and the gloss high compared with those of the fresh counterpart. Such a tendency was more or less found in all the films, as can be seen from the relative hazes and relative glosses. This finding clearly indicates that the extrusion shearing causes a variation in haze and gloss of blown LDPE film.

TABLE II
Optical Properties of Blown Films and Extrusion Swelling and MI of Fresh and Processed Materials

Sample	Extruder passing frequency	Haze	Relative haze	Gloss	Relative gloss	Swelling ratio	MI
A	0	6.2	0.71	10.4	1.13	1.33	0.55
	5	4.4		11.7		1.25	0.67
B	0	15.2	0.35	4.7	2.02	1.55	0.56
	5	5.3		9.5		1.23	0.87
C	0	4.0	0.73	12.5	1.06	1.33	1.37
	5	2.9		13.2		1.29	1.49
D	0	4.6	0.70	12.1	1.07	1.35	1.96
	5	3.2		13.0		1.29	2.06
E	0	9.1	0.53	8.9	1.37	1.50	2.97
	5	4.8		12.2		1.37	3.25
F	0	7.5	0.77	10.7	1.15	1.45	7.96
	5	5.7		12.3		1.41	8.23

Fujiki[4] reported that recognizable changes appeared in the viscoelastic properties of LDPE melts and optical properties of the blown films when the materials were subjected to extrusion shearing, but no appreciable variations take place in their molecular structures during the extrusion. Such changes in the viscoelastic and the optical properties were more remarkable in highly long-chain-branched LDPE than in less branched LDPE. It is important to know whether or not variations in molecular structures take place during the extrusion shearing when considering the cause of the changes in the haze and gloss of the blown film. In this study the intrinsic viscosities of samples E-0 (fresh sample) and E-5 (extruded for the fifth time) are 0.914 and 0.917, respectively, when the measurements were performed at 135°C, using 1,2,4-trichlorobenzene as solvent. They are in good agreement within experimental error. This fact demonstrates that no change in the molecular structure occurs during the extrusion shearing. The same statement may be true for other materials, as can be inferred from previous work,[5] though no intrinsic viscosity measurement is performed for other materials in this study. We can finally say that the variation in the haze and gloss is due to a certain change in the cohesive state of the polymer molecules which originates from the extrusion shearing rather than reduction of molecular weight and/or transformations of branching due to scissions of polymer chains. The authors[4,5] have definitely shown that the memory of the shearing histories was ascribable to a certain change in the cohesive state of the molecules and that this effect is strongly dependent on LCB, MI, MWD, and/or M_w. If the variation in the haze and gloss originates in the memory effect of the material, it must also be dependent on PI.

Here, we express the variation in the haze and gloss in relative terms; for example, the variation is 0.71 in haze and 1.13 in gloss for sample A. On the other hand, the variation is 0.35 in haze and 2.02 in gloss for sample B having about the same MI and density as sample A but a different PI. This seems to indicate that the variations are expressed more appropriately as a function of PI than of MI and/or density.

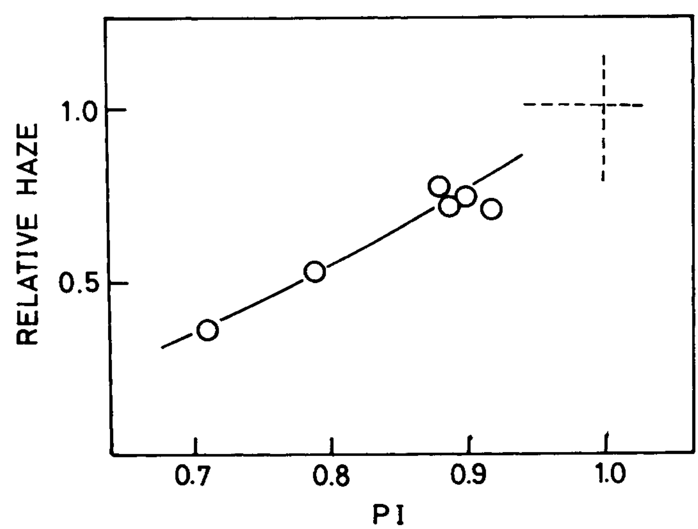

Fig. 1. Relationship between relative haze and processing index.

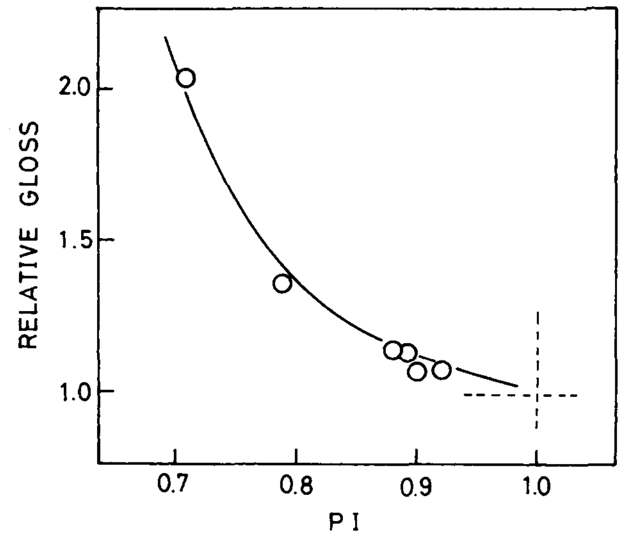

Fig. 2. Relationship between relative gloss and processing index.

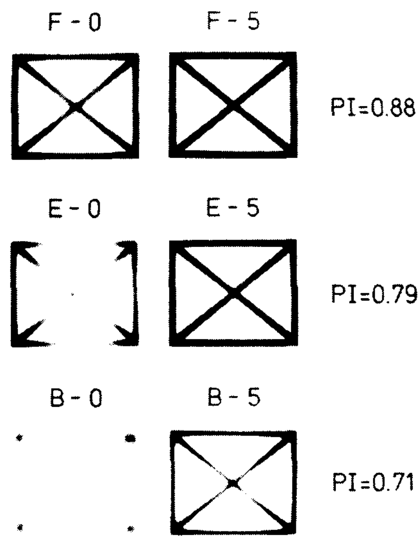

Fig. 3. Relationship between variation in transparency of blown films and processing index.

Figures 1 and 2 show the plots of the relative hazes and relative glosses against PI. As can be seen from the figures, when the PI approaches unity, both the relative haze and relative gloss tends to unity, too. This is visually shown in Figure 3 as the variation in transparency of the blown films made from fresh material and film extruded for the fifth time for samples B, E, and F. The photograph was taken through the three-layered blown films which were 20 cm away from the cross mark. These figures prove that relative haze and relative gloss are well expressed as a function of PI. Such finding shows that both the haze and gloss are controlled rather by an elastic response of the melt than by size of the crystallites and/or the crystallinity of the extruded film. The PI is also considered a measure which expresses the difference between the extent of elastic response of the melt for the fresh material and that for its sheared one. The authors have pointed out in a previous paper[4] that the overall haze of LDPE blown film might be controlled by the external haze which is attributed to surface roughness of the extruded film and is closely correlated to such viscoelastic properties as die swell and capillary end correction. The results obtained in this study further support our previous finding.

In conclusions, a recognizable variation in the optical properties of LDPE blown film occurs when the material is subjected to extrusion shearing, the extent of such variations can be accurately estimated from the PI introduced in the preceding paper[5] as a measure of the memory effect of the shearing histories of LDPE.

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