

Influence of Shearing History on the Rheological Properties and Processability of Branched Polymers.

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Synopsis

The influence of shearing history on the viscoelastic properties of low-density polyethylene (LDPE) is investigated. Swelling of extrudates from a melt indexer is measured for monitoring the variation in viscoelasticity. Continuous shearing of molten LDPE reduces the swelling ratio. The reduction is not due to molecular degradation, as evidenced by constancy of intrinsic viscosity. The rate of the reduction in the swelling ratio depends on the shearing conditions and characteristics of LDPE, but the swelling ratios finally attain a steady value. The swelling ratio reduced by the continuous shearing is completely recovered by solvent or heat treatment. The ratio of the completely reduced swelling ratio to the completely recovered one is defined as a new index representing the viscoelastic variation, the processing index (PI), and the relationship between PI and the primary molecular parameters of LDPE is investigated. It is concluded that the variation in the viscoelastic properties becomes more remarkable with increase in the weight-average molecular weight. The cause of the viscoelastic variation is also discussed from the rheological and thermodynamic points of view.

INTRODUCTION

Several papers¹⁻³ on anomalous viscoelastic behavior of branched polymers have been published for the last several years. In these articles the term "anomalous viscoelastic behavior" describes the following two notable phenomena: Firstly, when the branched polymers are sheared continuously, appreciable changes appear in their viscoelastic properties (e.g., an increase in melt flow rate, decrease in extrusion swelling, and reduction of surface roughness of extrudates), though no variation takes place in their primary molecular parameters such as molecular weight, molecular weight distribution, and the long-chain branching frequency during the shearing process. Secondly, the increased melt flow rate or the decreased extrusion swelling returns to its original value before the shearing by holding the shear-worked material in a molten state for several hours or by dissolving it in hot xylene and subsequently sucking the solvent with a vacuum pump.

Thus, we can say that long-chain branched polymers are able to memorize the shear working. Such memory effects are expected to play an important role in the processing of long-chain branched polymers, because the processability of polymeric materials naturally reflects their viscoelastic properties. The influence of the memory effects on the processability of low-density polyethylene (LDPE) will be discussed in a later paper. In addition, the studies on the memory effects are expected to make it possible for us to know about the nature of entanglements of long-chain branched polymers in more detail. A previous study³ carried out from the molecular structural and rheological points of view suggested that the memory effects were more remarkable in a highly branched LDPE than in a less

branched one. However, at the present stage of studies, little is known about the mechanism of the development of the anomalous behavior and the molecular structural parameters governing the memory effects of branched polymers.

The purpose of this paper is to investigate the relationship between the structural parameters and the memory effects of branched polymers by use of well-characterized LDPE resins.

EXPERIMENTAL

Nine LDPEs were used in this study. They were classified into the three families, A, B, and C, according to the polymerization conditions.

In general, it is said that the fine structure of LDPE depends on its polymerization conditions. It is difficult to know the fine structure of branches of LDPE in detail at the present stage of the characterization of branched polymers, but the structural parameters such as the number of branches per molecule can be determined by the combined use of gel permeation chromatography and intrinsic viscosity data. In this study the structural parameters for the materials were obtained on the basis of the method presented by Drott and Mendelson.⁴ It is presumed in their procedure that the long-chain branching frequency is independent of molecular weight. The following equations^{5,6} were used in this study:

$$[\eta] = 7.14 \times 10^{-4} M_w^{0.67} \quad (1)$$

for the relationship⁵ between the molecular weight and intrinsic viscosity of linear polyethylene and

$$G = g^{0.6} \quad (2)$$

for the confirmed relationship⁶ between G , the ratio of the intrinsic viscosity of a branched molecule to that of a linear one of the same molecular weight, and g , the ratio of the square of the radius of gyration of a branched molecule to that of a linear one of the same molecular weight. The intrinsic viscosities and gel permeation chromatograms were obtained at 135°C with 1,2,4-trichlorobenzene as solvent. The long-chain branching frequency, λ , the weight-average number of branches per molecule, n_w , and the weight-average molecular weight, M_w , of the materials are shown in Table I. Here, λ is defined by n_w/M_w .

The samples with various histories of the shear working were prepared by

TABLE I
Characteristics of the Materials

| Sample | Melt index | Density | $M_w \times 10^{-5}$ | $\lambda \times 10^4$ | n_w | PI^a |
|--------|------------|---------|----------------------|-----------------------|-------|--------|
| A-1 | 1.1 | 0.917 | 9.26 | 1.05 | 97.2 | 0.65 |
| A-2 | 3.3 | 0.916 | 6.03 | 1.23 | 74.2 | 0.67 |
| A-3 | 8.1 | 0.914 | 4.88 | 1.41 | 68.8 | 0.74 |
| A-4 | 22.6 | 0.915 | 3.89 | 1.70 | 66.1 | 0.79 |
| B-1 | 3.1 | 0.924 | 1.90 | 0.63 | 12.0 | 0.76 |
| B-2 | 7.8 | 0.924 | 1.60 | 0.81 | 13.0 | 0.85 |
| B-3 | 23.0 | 0.924 | 1.59 | 1.07 | 17.0 | 0.93 |
| C-1 | 4.5 | 0.928 | 1.08 | 0.38 | 4.1 | 0.85 |
| C-2 | 24.0 | 0.928 | 0.71 | 0.48 | 3.4 | 0.93 |

^a Processing index.

changing shear working time and shear working temperature. The shear working was performed with a Brabender plasticorder equipped with No. 5 rotor at 50 rpm rotor speed. Prior to the shearing with the Brabender, 500 ppm of 4,4'-thiobis(3-methyl-6-*tert*-butylphenol) was added to the materials in order to prevent them from thermal oxidation.

Solvent-treated materials were prepared by dissolving the Brabender-worked materials in hot xylene of 135°C and subsequently sucking the solvent with a vacuum pump at 160°C. Heat-treated materials were prepared by holding the Brabender-worked materials in the molten state. Heat treatment was carried out in a glass tube filled with nitrogen.

The first normal stress difference, $\sigma_{11} - \sigma_{22} = \Delta\sigma$, and shear stress, σ_{12} , were measured at 190°C with a Weissenberg rheogoniometer. The extrusion swelling was measured at 190°C with a melt indexer at an applied load of 2160 g. In this measurement the extrudate through the die was dropped into an aqueous solution of ethanol of the same density as that of the extrudate in order to prevent the effect of gravity on the swelling value.

RESULTS

The shear stress σ_{12} and the first normal stress difference $\Delta\sigma$ of the original sample A-1 are compared with those of the Brabender-sheared one in Figure 1. As is seen from this figure, both σ_{12} and $\Delta\sigma$ are appreciably reduced by the Brabender working for 60 min at 190°C. The variation in the viscoelastic properties of polymeric materials which results from the polymer processing is generally explained in terms of such a change in their primary structure as the reduction of molecular weight owing to the severance of polymer chains ordinarily observed in the mastication of rubbery materials, but the intrinsic viscosity is 1.127 for the unworked sample A-1 and 1.124 for the Brabender-worked sample. The variation in these intrinsic viscosities is within experimental error. These experimental results imply that no severance of polymer chains takes place but that some changes in the cohesive state of polymer molecules may occur during

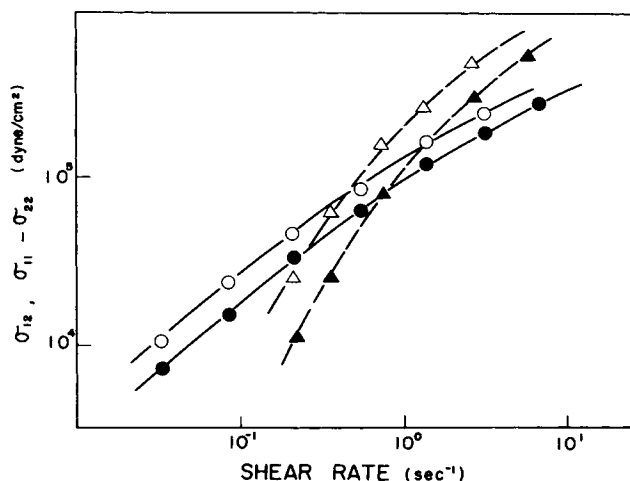


Fig. 1. Variation in shear stress and first normal stress difference for sample A-1 by Brabender working for 60 min at 190°C: (O) shear stress σ_{12} of original sample; (Δ) first normal stress difference $\Delta\sigma$ of original sample; (\bullet) σ_{12} of Brabender-worked sample; (\blacktriangle) $\Delta\sigma$ of Brabender worked sample.

the Brabender working. Such views were previously presented by Howells and Benbow,¹ Prichard and Wissbrun,² and Fujiki.³

However, at present little is known about the influence of the shearing history on the viscoelastic properties of branched polymers. Therefore, in the following experiments the author uses the swelling ratio as an index representing the viscoelastic changes and investigates the memory effects of LDPE in further detail. The swelling ratio is an elastic response of polymer melts and is very sensitive to the viscoelastic variation caused by the shear working. Figure 2 shows the relationship between the swelling ratio of sample A-3 and the shearing history represented in terms of the Brabender working time. Figure 3 is for sample A-1. As can be seen from these figures, the reduction of the swelling ratio depends on both the Brabender working time and temperature and also on the character of the materials. The swelling ratio of sample A-3 arrives at a steady value when the Brabender is operated for about 120 min at 190°C, but it cannot arrive at a steady value even after 180 min at 130°C. That is, as the working temperature increases the reduction in the extrusion swelling accelerates. On the other hand,

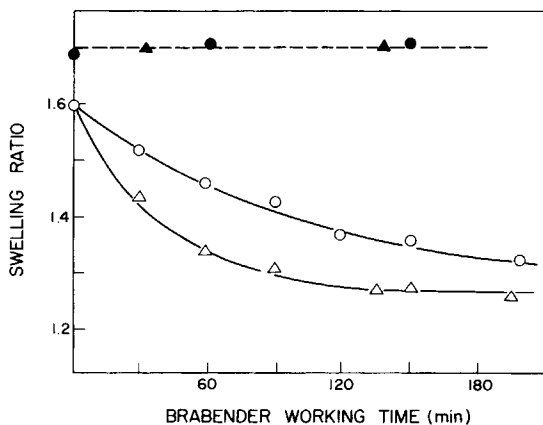


Fig. 2. Effects of shearing history on swelling ratio for sample A-3: (○) Brabender worked at 130°C; (Δ) Brabender worked at 190°C; (●,▲) solvent-treated sample.

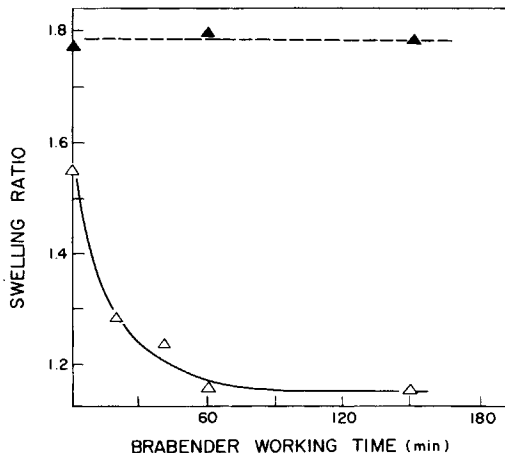


Fig. 3. Effect of shearing history on swelling ratio for sample A-1: (Δ) Brabender worked at 190°C; (▲) solvent-treated sample.

for sample A-1 the swelling ratio arrives at a steady value when the Brabender is operated for about 60 min at 190°C. Thus, the shearing conditions necessary for the swelling ratio to reach a steady value are dependent on the character of the material. However, when the Brabender is operated for at least 150 min at 190°C, the swelling ratios of all the materials arrive at steady values.

All the swelling ratios reduced by such shear working assume a constant value slightly higher than the swelling ratio of the unworked starting materials by means of solvent treatment as shown in Figures 2 and 3. For instance, the swelling ratio of the unworked sample A-1 is 1.55, that of the solvent-treated sample is 1.78 on the average, and the steady value is 1.14. Such behavior of the swelling ratios suggests that in the case of LDPE, the Brabender shearing or the extruding for pelletizing in manufacturing plants gives rise to some variation in the cohesive state of the polymer molecules without any changes in the primary molecular structure. If the shearing gives rise to some changes such as severance of the polymer chains and/or breakdowns of the branching structure, the swelling ratio once reduced cannot revert to the values of the dashed lines shown in Figures 2 and 3. The results of Figure 4 also support the idea described above. In this experiment, samples A-1 and A-3 undergo repeated shearing and solvent treatment, and no variation is detected in their primary molecular structure.

The recovery of the reduced swelling ratio is also accomplished by the heat treatment mentioned above. The relationships between the swelling ratio and the heat treatment time are shown in Figures 5 and 6. These experiments are especially focused on the effects of the heating temperature and characteristics of the material on the recovering of the reduced swelling ratio. Sample A-4 has a reduced swelling ratio of 1.32 and the swelling ratio after solvent treatment is 1.60, as shown in Figure 5. Here, if characteristic holding time is defined by the time required for the achievement of complete recovery of the reduced swelling ratio, holding time is about 360 min for sample A-4 when the heat treatment is carried out at 130°C, but is about 150 min at 190°C. That is, the recovery rate of the swelling ratio increases with increase in the heating temperature. On the other hand, the characteristic holding time at 190°C clearly depends on some characteristics of the materials as shown in Figure 6.

Here, in order to consider the results of Figure 6, the author defines a new parameter, the processing index (PI), which represents the degree of variation in the viscoelastic properties caused by the shear working. PI is defined by the ratio of the completely reduced swelling ratio to the completely recovered one

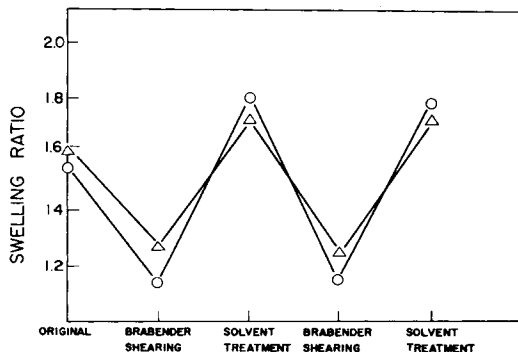


Fig. 4. Reversible change in swelling ratio for sample A-1 (O) and A-3 (Δ) by repeated shearing and solvent treatment.

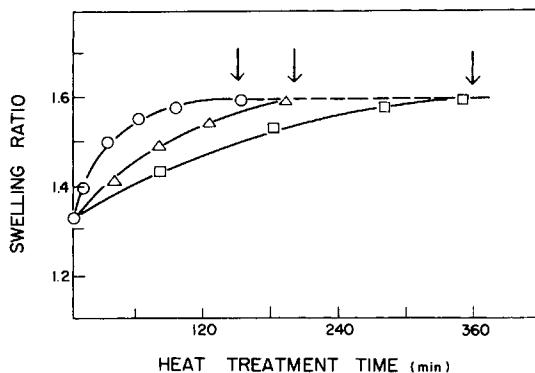


Fig. 5. Recovery of swelling ratio for sample A-4 by heat treatment at various temperatures: (□) 130°C; (Δ) 160°C; (○) 190°C. Arrows indicate characteristic holding times.

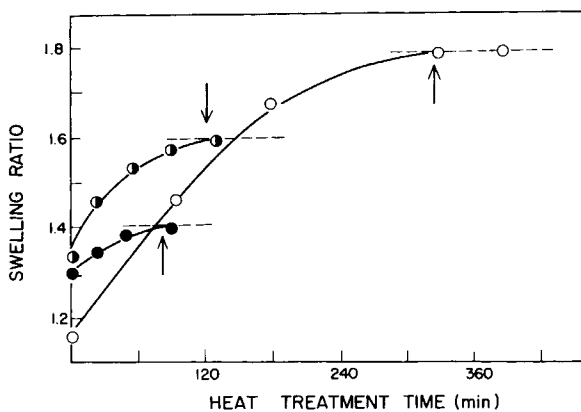


Fig. 6. Recovery of swelling ratio by heat treatment at 190°C: (○) sample A-1; (◐) A-4; (●) B-3.

by means of solvent treatment or heat treatment. When PI is unity, the viscoelastic properties of the material are not influenced by the shear working; but when it is less than unity, a variation in viscoelastic properties takes place. Figure 7 shows the relationship between PI and the characteristic holding time at 190°C for all the materials. The characteristic holding time bears a linear relation to PI and increases with decrease in PI .

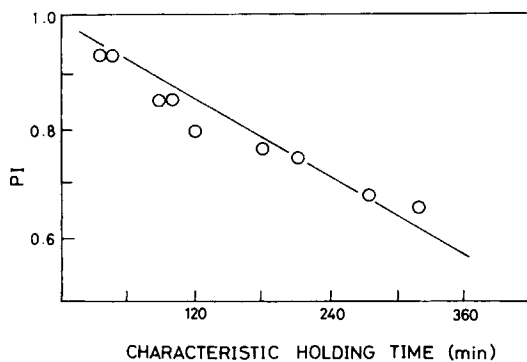


Fig. 7. Processing index vs characteristic holding time at 190°C.

Finally, the relationship between PI and the structural parameters of LDPE are investigated. Figure 8 shows the plots of PI versus the long-chain branching frequency, λ . In Figure 9, PI is plotted against the weight-average molecular weight, M_w . As can be seen from Figure 8, the relationship between PI and λ is complicated. That is, if melt index is taken as a parameter, PI decreases with increase in λ . However, if the polymerization conditions are taken as a parameter, PI increases with increase in λ . At present it is not possible to interpret with any certainty the results of Figure 8 from the molecular structural point of view, therefore only the experimental results are shown here. On the other hand, Figure 9 shows that PI decreases with an increase in M_w , and M_w increases with an increase in n_w as can be seen from Table I. Consequently, it is concluded that the variation in the viscoelastic properties of LDPE caused by the shearing becomes more remarkable with increase in M_w accompanying an increase in n_w .

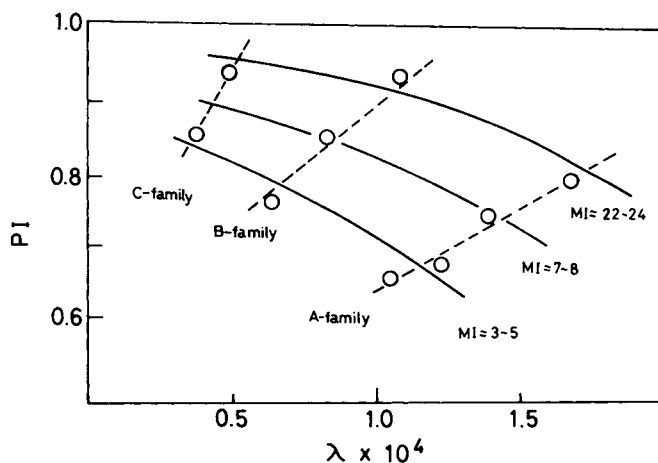


Fig. 8. Processing index vs long-chain branching frequency.

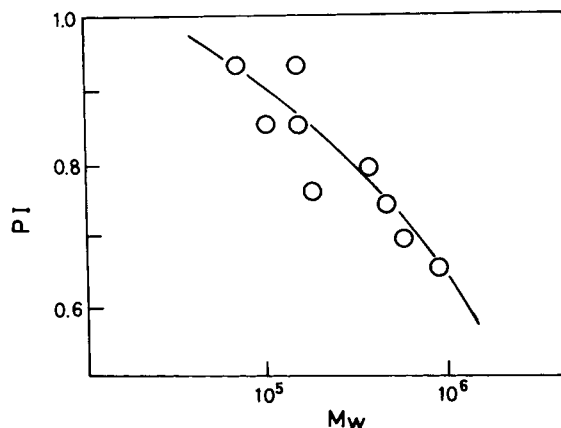


Fig. 9. Processing index vs weight-average molecular weight.

DISCUSSION

At present, the memory effects of LDPE described above can be interpreted in two ways. One is based on the viscoelastic consideration of long-chain branched polymers. In general, two types of entanglements⁷ are considered for long-chain branched polymers: one presumably occurs between the branches; another is assumed to arise from looping and coiling of the main chains at the branching points. In a shear field, the former entanglement may comparatively easily entangle or disentangle under a process,⁸ an explanation offered by Graessley in order to interpret a non-Newtonian viscosity of polymeric materials, but the latter do not so easily entangle or disentangle because of steric hindrance at the branching points. As a result of such kinetics of the entanglement process of the latter, the flow unit⁹ proposed by Busse, which probably consisted of a few molecules, may be formed for long-chain branched polymers. However, the entanglement density seems to be gradually reduced by the continuous shearing, the flow unit may be subdivided, and hence the viscoelastic variation shown in Figures 2 and 3 takes place. On the other hand, the recovery of the reduced swelling ratio by means of the solvent treatment is naturally ascribed to the reentanglement between the main chains at the branching points in the solution. Heat treatment also produces recovery of the reduced swelling ratio, but in this case the complete recovery may require a long time because the entanglement process is depressed in the melt as compared with the solution. According to such viscoelastic considerations, the experimental findings derived from the results of Figures 7 and 9, where the time required for complete recovery of the swelling ratio increases with increase in M_w , may imply that the material with higher M_w forms the entanglement with more complicated steric hindrance.

Another explanation is based on thermodynamic information recently obtained. Several investigators^{10,11} reported that surface tension of LDPE is clearly different from that of HDPE. This fact suggests that the thermodynamic quantities of long-chain branched polymers may be dependent on the fine structure of the long-chain branching. LDPE is generally composed of polymer species with various fine structures of branches. Therefore, it is assumed that LDPE may consist of the polymer species with different thermodynamic quantities and, as a result, phase separation may occur. When the long-chain branched polymer is sheared, the coagulation formed as a result of the phase separation may be subdivided and the newly formed phase surface may make the thermodynamic state of the material metastable. Reversely, the solvent or heat treatment reconstructs the coagulation and makes the material most thermodynamically stable. Such variation in the size of the coagulation is considered to be the cause of the memory effects of LDPE. One of my collaborators³ previously presented the above idea on the basis of the thermodynamic considerations.

In conclusion, LDPE can memorize shearing history, and the variation in the viscoelastic properties of LDPE caused by the shearing process becomes more pronounced with increase in M_w accompanying an increase in n_w . The cause of the memory effects is also discussed from the rheological and thermodynamic points of view.

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