Influence of Shearing History on the Rheological Properties and Processability of Branched Polymers. III. An Amorphous Long-Chain Branched Polymer

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Synopsis

Viscoelastic properties of branched polymers vary with their shearing history; notwithstanding, their primary molecular parameters do not change. According to a recent study, such viscoelastic variation was believed to be observed only with crystalline long-chain branched polymers such as low-density polyethylene or polyacetal. That is, the origin of the viscoelastic variation was attributed to the presence of specific entanglements at the branching points, which was formed during the crystallization process. However, the viscoelastic variation of the long-chain branched polymers is the phenomenon at temperatures well above their melting points, namely, it is considered that whether the long-chain branched polymers are crystalline or not is not essential for the occurrence of the viscoelastic variation. Thus, the influence of the shearing history on the rheological properties of an amorphous long-chain branched polymer was investigated in this paper, and it was found that, irrespective of their crystallinity, the viscoelastic properties of long-chain branched polymers vary according to their shearing history.

INTRODUCTION

In two previous papers[1,2] the authors have reported that (i) low-density polyethylene (LDPE) was characterized by a "memory" of shearing histories during shear processing such as extrusion processing or Brabender working[4]; (ii) this character of the material was strongly dependent on long-chain branching (LCB) frequency, melt index (MI) and shape of molecular weight distribution (MWD), and/or weight-average molecular weight (M_w) and it exerts a great influence on rheological properties and end-use properties; (iii) such memory could vanish from the material by holding the processed material in a molten state for several hours (the heat treatment) or dissolving it in hot xylene and subsequently taking off the solvent by evaporating it under a hot nitrogen atmosphere[3] or reduced pressure[2] (the solvent treatment). As can be seen from the previous papers[1,2] the development of such memory effect of LDPE originates from a certain change in the cohesive state of the material, not from variations in primary molecular parameters such as abscission of the polymer chains and/or branches caused by the shear processing. In the present stage of studies on the subject there are no corroborative interpretations on the mechanism of such phenomenon, but some speculative explanations for them are presented by some investigators. Prichard and Wissbrun[5] investigated a memory effect of acetal polymers and speculated that such phenomena were caused by disruption of entanglement networks of polymer chains owing to continuous shearing of the materials and by their voluntary reforming which was achieved by holding the sheared polymer in the molten state for several hours or by dissolving it in a good solvent

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and reprecipitating it. According to their speculation the memory effect is considered to be pronounced in the crystalline long-chain branched polymers but absent in linear analogs or amorphous long-chain branched polymers. That is, they attributed the memory effect to the fact that exceptionally strong entanglement networks, once disrupted by shearing, were reformed at the branching points when the sheared polymer crystallized. However, it should be noted that such memory effect is the phenomenon at temperatures well above the melting points of the materials.[1-5] As pointed out in the previous papers[1,2] the authors considered that the presence of long-chain branching is essential for the development of the memory effect, but it is not always clear whether the crystallizability of long-chain branched polymers should be required for that or not because no sufficient experiments have been performed for verification of this subject.

The object of this paper is to investigate this problem, using an amorphous long-chain branched polymer.

EXPERIMENTAL

The material used in this study was ethylene-vinylacetate (EVA) copolymer with 79.0% by weight of vinylacetate, SOARLEX FH, which was obtained by a suspension polymerization process and supplied by Nippon Synthetic Chemical Industry Co., Ltd. The crystalline region of EVA copolymer is generally below 43% to 50% by weight of vinylacetate content,[6] and consequently we can say that the material is an amorphous polymer. The glass transition point of the material measured on a dilatometer was 1°C. Melt index and density at 25°C of the material are 27.5 g/10 min and 1.1283 g/ml. Here, MI was measured according to ASTM D 1238-73 (procedure A) and density was measured on the dilatometer.

In general, EVA copolymer has two kinds of LCB which are different in the process of their formation. One originates from the chain transfer reaction of the polymer to the hydrogen atom of methylene in the principal chain and another to the methyl group of vinylacetate. Especially, since the latter is severed from the principal chain by saponifying the polymer, we can obtain the amorphous polymer near to the linear analog by completely saponifying the material and subsequently acetylating the saponified one. In this study the saponification was carried out according to the specification of B.P. 634,140 applicated by I.C.I and the acetylation of Hermann and Haehnel.[7] The material obtained in this manner was referred to as RFH. As can be seen from the reaction paths above mentioned, samples FH and RFH are different from one another in their number of LCB but identical in their chemical composition. In fact, vinylacetate content of sample RFH was also 79.0% by weight.

The number of LCB from the methyl group of vinylacetate per molecule of sample FH (n) can be calculated from the following equation

$$n = \frac{M_n \text{ of sample FH}}{M_n \text{ of sample RFH}} - 1.0 \tag{1}$$

where M_n is the number-average molecular weight. The measurement of M_n of both the materials was performed at 30°C with Hallikainen membrane osmometer (Model 1361), using a gel cellophon membrane No. 600, supplied by

Carl Schleicher and Schnell Corp. and methanol as a solvent. M_n obtained in this manner is 114,700 for sample FH and 31,400 for sample RFH, and consequently n is 2.65.

Molecular weight distributions of the materials were measured with Waters gel permeation chromatograph with a four-column Styragel combination of 10^3, 10^4, 10^5, and 10^6 Å. The instrument was operated at 135°C and 1 ml/min of the eluent flow rate, using 1,2,4-trichlorobenzene as an eluent solvent.

The shearing history was given to the material by shearing it with Brabender plasticorder with No. 5 rotor and its magnitude was controlled by Brabender working time. The Brabender working was performed at 100°C of the kneading temperature and 50 rpm of the rotor speed. In this study 2000 ppm of an antioxidant, 4,4'-thiobis (6-ter-butyl-m-cresol), was added to the materials prior to the Brabender working in order to prevent them from thermal oxidation. Vanishing of the shearing history from the Brabender-worked materials was achieved by two procedures—the solvent treatment and the heat treatment. The solvent treatment was carried out by means of dissolving the Brabender-worked materials in hot xylene at 100°C, and subsequently sucking the solvent at 150°C with a vacuum pump. The heat treatment was carried out by means of the procedure described in detail in the previous paper.[2]

The extrusion swelling of the extrudate was measured with a capillary rheometer, Kōka flow tester manufactured by Shimadzu Co., Ltd., equipped with a flat die of length to radius (L/R) 36.0. The extrusion was carried out at 130°C and 20 kg/cm² of the extrusion pressure for sample FH and at 80°C and 100 kg/cm² for sample RFH, and a photographic technique was employed for the diameter measurement of the extrudates.

RESULTS AND DISCUSSION

Figure 1 shows GPC chromatograms of samples FH and RFH. As can be seen from the figure, MWD of sample FH is surprisingly broad due to the presence of LCB. On the other hand, that of sample RFH is narrow because of the absence
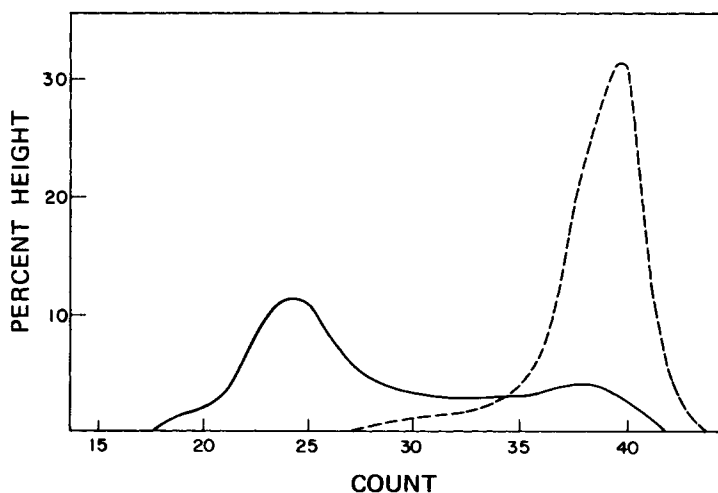

Fig. 1. GPC chromatograms of FH and RFH: (—) FH; (- - -) RFH.
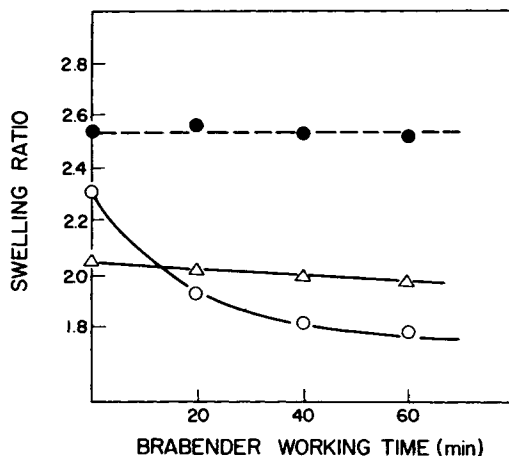
Fig. 2. Effect of shearing history on swelling ratios for FH and RFH: (○) FH; (△) RFH; (●) solvent-treated FH.
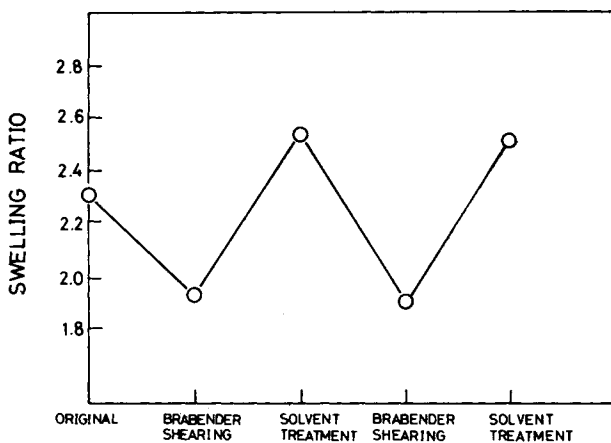

Fig. 3. Reversible change in swelling ratio for FH by repeated Brabender working and solvent treating.

of LCB from acetoxy groups. The LCB from methylene sequence is severed by neither saponification nor the subsequent acetylation. Therefore, the slight tailing of GPC chromatogram of sample RFH seems to be attributed to the presence of polyethylene type LCB.

In the following experiments, the memory effect of the highly branched material FH, and the less branched one RFH, will be investigated. Figure 2 shows the influence of shearing history on the swelling ratios of the materials. The swelling ratio of the less branched material RFH is little influenced by the shear working, but the swelling ratio of the highly branched one FH decreases with an increase in the Brabender working time and seems to reach a steady value. In addition, all the swelling ratios of sample FH reduced by the Brabender working assume the constant value slightly higher than that of the unworked sample FH by means of the solvent treating as indicated by the dashed line with the closed circles. Such behavior of the swelling ratios of sample FH is the same as that of LDPE described in the previous paper,[2] and, therefore, it is clear in
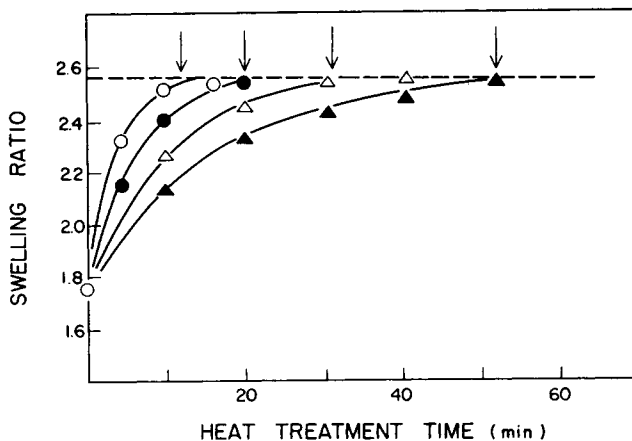
Fig. 4. Recovery of swelling ratio for FH by heat treating at various temperatures: (▲) 120°C; (△) 130°C; (●) 140°C; (O) 160°C.

this polymer system that no variation takes place in its primary molecular parameters such as LCB frequency, M_w and MWD, but some variation takes place in the cohesive state of polymer chains during the Brabender working and solvent treating. If the Brabender working gives rise to some changes such as severence of the polymer chains, the swelling ratio once reduced cannot revert to the dashed line shown in Figure 2. According to such an idea, the difference in the swelling ratios between the original FH and the solvent treated ones is attributed to the fact that the shear working is applied to the original material for its shaping in manufacturing plants. Figure 3 also supports the idea described above. In this experiment, sample FH undergoes the repeated Brabender working and solvent treating.

The recovery of the reduced swelling ratio is also accomplished by the heat treating. Figure 4 shows the relationship between the swelling ratio for 60 min Brabender worked FH and the heat treating time at various temperatures. The recovery rate of the swelling ratio increases with an increase in the heating temperature. The results suggest that the recovery of the cohesive state, once disrupted by the shear working, is directly related to the macro-Brownian motion of polymer chains.[2]

In conclusion, the memory effect is observed with an amorphous long-chain branched polymer, and therefore the cause of the memory effect is not attributable to the exceptionally strong entanglements created at the branching points when the material crystallizes, but to the presence of long-chain branching itself.

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