

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

IV. Capillary Flow and Die Swell of Low-Density Polyethylene

MINORU ROKUDAI and TOKIO FUJIKI, *Tokyo Research Laboratories, Toyo Soda Manufacturing Company, 2743-1, Ayase-shi, Kanagawa-ken, Japan*

Synopsis

Low-density polyethylene (LDPE) melts show anomalous rheological behavior; their viscoelastic properties vary with their shearing histories although their molecular structural parameters do not change. Capillary flow and die swell behavior were dependent not only on the experimental conditions such as temperature or shear stress but also on the processing index (PI), which was introduced in a preceding article in order to quantify the anomalous rheological behavior of LDPE melts. In addition, it was found that the flow activation energy at constant shear stress also varied with the shearing histories. The experimental findings are discussed in terms of the rheological flow units of LDPE melts.

INTRODUCTION

It is well known that viscoelastic properties of linear polymers are dependent on such molecular structural parameters as weight-average molecular weight (M_w) and molecular weight distribution (MWD). Those of long-chain branched polymers such as low-density polyethylene (LDPE) or branched polyacetal,¹ however, are dependent on not only their molecular structural parameters but also their shearing histories. Several articles¹⁻⁴ have reported that (1) melt viscosity and die swell of LDPE are reduced by extruding or Brabender shearing, though no variation takes place in their molecular structural parameters during the processing; and (2) the reduced melt viscosity and elasticity spontaneously return to the same or slightly higher values than those of unprocessed material by holding the processed material in a molten state for several hours (heat treatment) or by dissolving it in a good solvent and subsequently removing the solvent from the materials under reduced pressure (solvent treatment). That is, two limits of a material state in LDPE exist. One is obtained by heat or solvent treatment of unprocessed or processed materials and another by extrusion shearing or roller kneading such as Brabender shearing of the materials in a molten state until no further reduction is detected in melt viscosity or die swell.⁴ In this report we designate the materials obtained by the former as solvent- or heat-treated materials and the materials obtained by the latter as full-sheared ones. These experimental facts demonstrate that it is indispensable to identify the shearing histories of the materials for analysis of rheological behavior of LDPE, although most of the studies⁵⁻⁸ on melt rheology of LDPE carried out in the past did not take into consideration the effects of shearing history on the rheological properties.

The object of this study was to investigate the effects of the shearing histories on capillary flow behavior and die swell properties of LDPE, using well-identified materials as to shearing history and molecular structural parameters.

EXPERIMENTAL

Materials

Three LDPEs were used in this study. Their long-chain branching frequency (λ), M_n , and M_w are tabulated in Table I. These molecular structural parameters were determined from the GPC chromatogram and the intrinsic viscosity of the materials using the following equations presented by Kurata and co-workers⁹ for randomly branched polymers:

$$G = g^{0.6} \quad (1)$$

$$g = \left[\left(1 + \frac{\lambda M}{7} \right)^{1/2} + \frac{4\lambda M}{9\pi} \right]^{-1/2} \quad (2)$$

where G is the ratio of the intrinsic viscosities of branched and linear molecules having the same molecular weight and g is the corresponding ratio of the square radii of gyration. Both the GPC operation and the intrinsic viscosity measurement were carried out at 135°C using 1,2,4-trichlorobenzene as solvent. According to Cervenska,¹⁰ eq. (3) gives the best relationship between the intrinsic viscosity $[\eta]$ and molecular weight M of linear PE when the measurement is performed under the above-mentioned experimental conditions:

$$[\eta] = 4.48 \times 10^{-4} M^{0.718} \quad (3)$$

The solvent-treated materials were prepared dissolving the untreated materials in xylene at 135°C and subsequently removing the solvent with a rotary vacuum pump at 160°C. (Here, untreated material means commercially available LDPE pellets.) The full-sheared materials were prepared by shear kneading the untreated materials with a Brabender plasticorder equipped with a No. 5 rotor at 50 rpm for 150 min at 190°C. Prior to the Brabender shearing, 2000 ppm of an antioxidant, 4,4'-thiobis(3-methyl-6-*ter*-butylphenol), was added to the materials in order to protect them from thermal oxidation.

In a previous report⁴ a new LDPE characterizing index named the processing index (PI) was introduced in order to quantify the degree of variation in melt viscosity or die swell of LDPE caused by such continuous shearing as extruding or Brabender shearing. The PI was defined by the ratio of die swell of the full-sheared material to that of the solvent-treated one. Therefore it has the following character: If the rheological properties are not influenced at all by the shear processing, its PI is unity; but if the variation in the viscoelastic properties of LDPE takes place during the shear processing, its PI is less than unity. The die swell measurements were performed with a melt flow indexer at 190°C and applied load of 2160 g for determining sample PI. The results are shown in Table I.

TABLE I
 Characteristics of the Materials

Sample No.	Melt index	Density	$M_w \times 10^{-5}$	$\lambda \times 10^4$	M_w/M_n	PI
A-0	0.6	0.919	5.31	6.9	17.0	0.58
A-3	8.1	0.914	3.35	12.2	27.7	0.74
C-2	24.0	0.928	0.67	2.1	7.4	0.93

Capillary Flow

The capillary flow measurements were performed with an Instron capillary rheometer model 3211 in the temperature range of 130 to 228°C using five tungsten carbide capillaries 0.0502 in. in diameter and 5.05, 10.12, 20.09, 33.79, and 59.83 in L/D , with 90° tapered entrance angle.

For steady shear flow of polymer liquids in a capillary of diameter D and length L , the apparent shear stress σ_w and the apparent shear rate $\dot{\gamma}_w$ at the capillary wall are obtained by the equations

$$\sigma_w = P_t D / 4L \quad (4)$$

and

$$\dot{\gamma}_w = 32Q / \pi D^3 \quad (5)$$

where Q is the volumetric flow rate and P_t is the applied pressure difference across the ends of the capillary. The true shear stress σ_{tw} at the wall is calculated by the slope of the following equation:

$$P_t = 2\sigma_{tw}(2L/D + e) \quad (6)$$

where e is the total end correction. The true shear rate $\dot{\gamma}_{tw}$ is obtained by the equation¹¹

$$\dot{\gamma}_{tw} = [(3N + 1)/4N]\dot{\gamma}_w \quad (7)$$

where

$$N = d \log \sigma_{tw} / d \log \dot{\gamma}_w \quad (8)$$

As mentioned above, the melt viscosity and elasticity of the sheared materials return to the values they had before shearing by merely holding them in a molten state. The rheological properties of the full-sheared materials were therefore measured within 15 min in order to minimize the effect of a thermal recovery on the viscosity.

Inasmuch as the rheological properties of LDPE are changed by the shear processing such as Brabender shearing as mentioned above, it is expected that the viscoelastic properties of the materials are changed by the additional shear applied to the materials during the capillary flow experiments. The following experiment was made in order to check the expectation. The solvent-treated material of sample A-0 with the smallest PI was extruded from a capillary with an $L/D = 59.83$ at 190°C, and both the apparent shear stress σ_w and the swell ratio at $\dot{\gamma}_w = 35.0 \text{ sec}^{-1}$ were measured. The extrudates were collected and σ_w and the swell ratio were measured again. These measurements were repeated five times. The results are tabulated in Table II. Although the swell ratio slightly decreases, no variation in σ_w is detected. This finding indicates that

TABLE II
Influence of Extruding on Rheological Properties of the Solvent-Treated Sample A-0

	Pass Frequency					
	1	2	3	4	5	6
$\sigma_w \times 10^{-5}$, dyn/cm ²	6.84	6.86	6.86	6.86	6.84	6.86
Swell ratio	1.515	1.510	1.506	1.507	1.502	1.493

a variation in the viscoelastic properties of the solvent-treated materials occurs during the capillary flow measurement but is negligibly small.

RESULTS

In Figure 1, the logarithms of σ_{tw} are plotted against the logarithms of $\dot{\gamma}_{tw}$ for the respective solvent-treated and full-sheared materials of three samples, A-0, A-3, C-2, and untreated sample A-0. As is seen from this figure, clear differences in σ_{tw} are found between the solvent-treated and the full-sheared samples A-0 and A-3 but no difference is found between treatments of sample C-2 when compared at a given shear rate. This result indicates that (1) Brabender shearing or solvent treatment makes such a difference and (2) the degree of the differences in σ_{tw} is dependent on PI of the samples.

Figures 2(a) and 2(b) show the relationship between melt viscosities and the reciprocal of absolute temperatures for the solvent-treated and the full-sheared materials of sample A-0. The melt viscosities (η) were calculated from the shear stress obtained by use of a capillary of $L/D = 59.83$ (σ_w) and $\dot{\gamma}_{tw}$ because the differences between σ_w and σ_{tw} were within 5% according to the results of Figure 1. As is seen from Figure 2(a), a good linear relationship is established between $\log \eta$ and $1/T$ over the temperature range from 130 to 228°C for the solvent-treated material, but no such relation holds in a higher temperature range for the full-sheared one [see Fig. 2(b)]. In the previous report,⁴ the authors clarified that the thermal recovery of melt viscosity and die swell of full-sheared LDPE

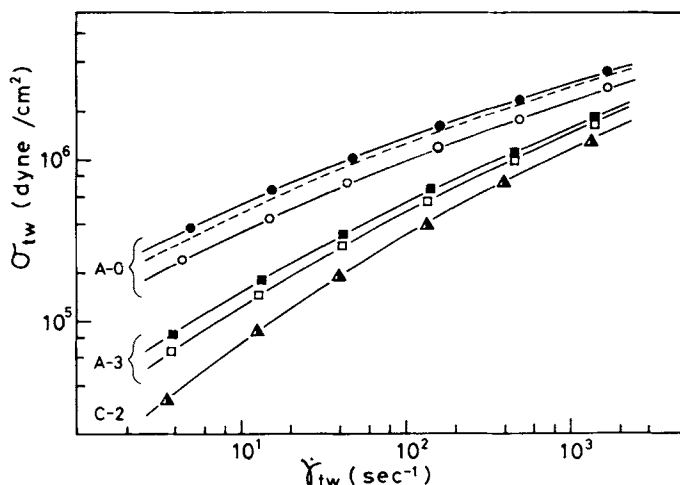
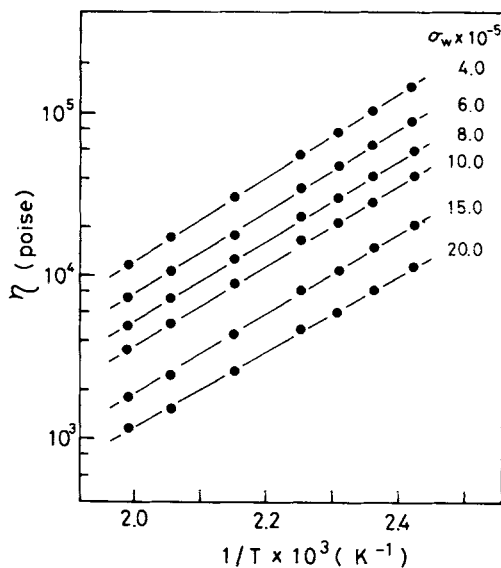
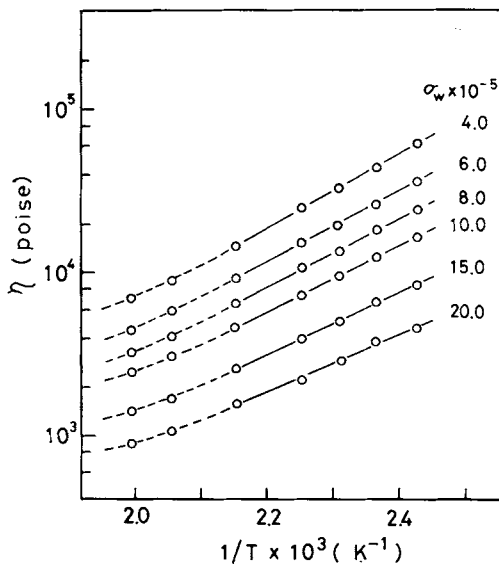


Fig. 1. Flow curves of LDPEs with different shearing histories at 160°C: (●, ■, ▲) solvent-treated materials; (○, □, △) full-sheared materials; (- -) untreated materials of sample A-0.



(a)



(b)

Fig. 2. (a) Relationship between $\log \eta$ of solvent-treated A-0 and $1/T$. (b) Relationship between $\log \eta$ of full-sheared A-0 and $1/T$.

is accelerated with increase in temperature. It may be acceptable, therefore, to consider that a failure of the linear relationship between $\log \eta$ and $1/T$ for the full-sheared material in the higher temperature range is attributed to a thermal recovery of the melt viscosity induced by heating of the material in the course of the viscosity measurement. If thermal recovery of the viscosity had not occurred, the Arrhenius plots of the full-sheared material would be linear.

Figure 3 shows plots of flow activation energies (E_a) versus the apparent shear

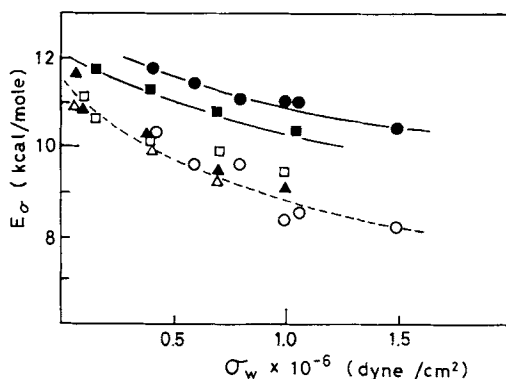


Fig. 3. Flow activation energy at constant shear stress: (●, ■, ▲) solvent-treated materials; (○, □, △) full-sheared materials.

stress σ_w for the respective solvent-treated and full-sheared materials of the three samples. Here, the values of E_σ of the full-sheared materials were calculated from the slopes of the linear portion of their $\log \eta-1/T$ relations. In this figure, filled circles, filled squares, and filled triangles designate the solvent-treated materials of samples A-0, A-3, and C-2, respectively, and open symbols, the corresponding full-sheared materials. The values of E_σ of the solvent-treated materials are clearly dependent on the characters of the samples (PI); E_σ of the solvent-treated material of sample A-0 is the highest, that of C-2 is the lowest, and that of A-3 is intermediate between those of A-0 and C-2. On the other hand, the values of E_σ of the full-sheared materials are independent of kind of sample and are the same as those of the solvent-treated materials of sample C-2 having a PI of 0.93, although Figure 3 shows some scatter. This finding is very interesting and is discussed later.

Plots of swell ratios for sample A-0 versus L/D at 190°C are shown in Figure 4. In this figure, filled circles indicate the onset of slight melt fracture. The swell ratio of the solvent-treated material is always larger than that of the full-sheared one, that is, the solvent-treated material is more elastic than the full-

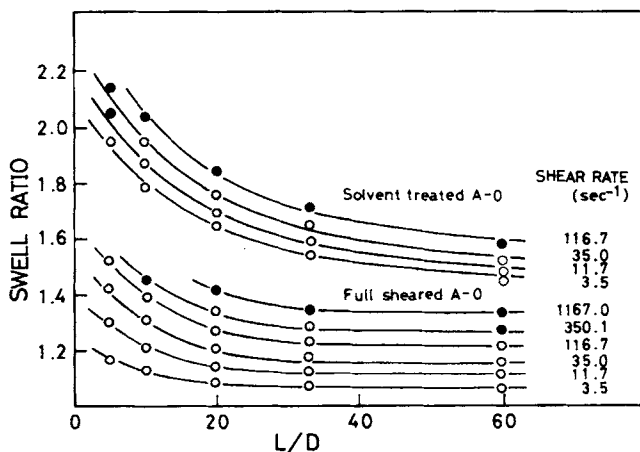


Fig. 4. Die swell behavior of sample A-0.

sheared one. The swell ratio of the solvent-treated material decreases with increase in L/D but does not attain a steady value even if a very long capillary ($L/D = 59.83$) is used. On the other hand, the swell ratio of the full-sheared material reaches a steady value at L/D of about 40. The swell ratio of the solvent-treated material of sample C-2 with the largest PI also does not attain a steady value, nor does the die swell behavior of the solvent-treated material of sample A-0. According to our investigation on the melt rheology of LDPE, sample A-0 belongs to a group of LDPEs with the smallest PI and sample C-2 to a group of LDPEs with the largest PI. We may, therefore, say that generally the swell ratios of the solvent-treated LDPEs do not attain steady values even if a considerably long capillary ($L/D = 59.83$) is used.

In Figure 5, the swell ratios measured using a capillary of $L/D = 59.83$ were plotted against $\dot{\gamma}_w$. It is clear that the die swell behavior of LDPE melts are greatly influenced by the shearing histories of the samples, and the degree of the influence of the shearing histories on the die swell behavior is clearly dependent on sample PI.

DISCUSSION

An experimental finding in this paper is that the capillary flow and die swell behavior of LDPE melts are dependent not only on the experimental conditions such as temperature or shear stress but also on the character of the samples (PI) and their shearing histories. The experimental fact shown in Figure 3 is especially interesting; the flow activation energies of the solvent-treated materials at constant shear stress are dependent on PI of the samples, but those of the full-sheared materials are independent of the kind of sample and are the same as that of the solvent-treated material of sample C-2 having a PI of 0.93.

In previous reports^{3,4} we discussed the cause of the variation in the viscoelastic

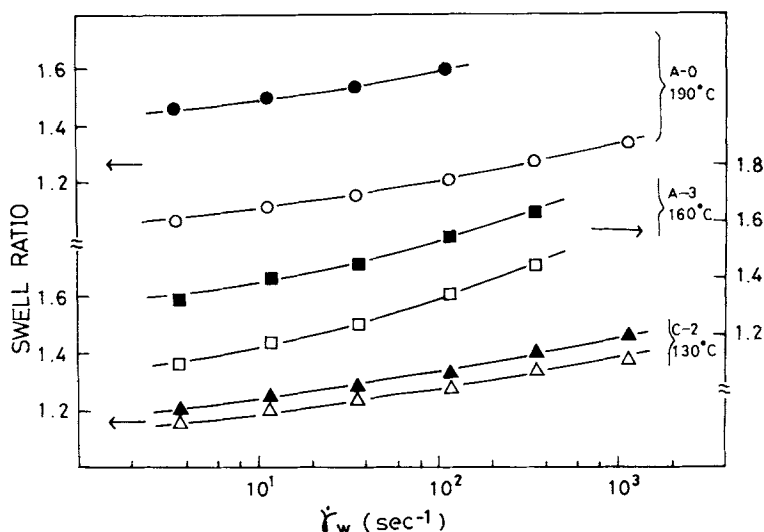


Fig. 5. Die swell behavior of LDPEs with different shearing histories: (●, ■, ▲) swell ratios of solvent-treated materials measured with a capillary ($L/D = 59.83$); (○, □, △) swell ratios of full-sheared materials measured with a capillary ($L/D = 59.83$).

properties of LDPE melts induced by the shear processing from the standpoint of a change in the size of the rheological flow units, which were often proposed in order to interpret the rheological properties of branched polymers.¹² If this speculation is true, the sample with small PI may form large flow units and the sample with large PI, small flow units when those samples are subjected to solvent or heat treatment. But when the samples are subjected to shear treatment, the flow units may gradually be destroyed by the shear processing and finally be subdivided or disappear. At the present stage of studies of melt rheology, it is difficult to discuss the magnitude of the flow activation energy from the molecular structural points of view, but it can be considered that the size of the flow units affects the magnitude of the flow activation energy. In other words, the flow activation energy of the solvent-treated material of a sample with small PI is larger than that of the solvent-treated material of a sample with large PI or the full-sheared materials. The results in Figure 3 strongly support this speculation.

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