

Relationship Between Processing History and Rheological Properties During Postprocessing Annealing for Anomalous Polyethylene Blends

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ABSTRACT: The effect of applied processing history and postprocessing annealing treatment on the rheological properties has been studied for a binary blend composed of linear low-density polyethylene (LLDPE) and low-density polyethylene produced by radical polymerization (LDPE). It has been found that intensive processing in an internal mixer depresses oscillatory modulus, especially storage modulus, at lower frequency region for LDPE and the blends with LLDPE, whereas the rheological properties of LLDPE are independent of both processing and annealing procedures. Further, the depression of the modulus is found to be more prominent for the blends with 20–40 wt % of LLDPE than

that for the pure LDPE, although the phenomenon is ascribed to conformation change of long-chain branches. Moreover, the blends show slower recovery of the modulus during the postprocessing annealing than do LDPE. The results demonstrate that processing and mixing conditions have to be considered seriously for LDPE/LLDPE blends showing enhanced melt elasticity. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1078–1083, 2006

Key words: polyethylene; blends; rheology; branched polymer; shear modification

INTRODUCTION

Polymers having long-chain branches show high melt elasticity, such as strain recovery after cessation, strain-hardening in elongational viscosity, normal stress difference, and so on. The magnitude of melt elasticity, however, largely depends on the processing and thermal history, which has been known as “shear modification.”^{1–15} Even without molecular scission, applied flow or processing history depresses elastic properties rather than viscous ones, which is, of course, responsible for the processability. The sample having more intense processing history shows higher extensibility,^{6,9} higher critical shear rate for the onset of melt fracture,^{11,14} and optical transparency due to the reduction of surface roughness.^{2,3,7,9} Further, annealing procedure above the melting point or solvent-treatment enhances the melt elasticity again to the original, equilibrium state. Münstedt⁶ explained the mechanism from the molecular point of view based on tube model developed by Doi and Edwards.¹⁶ According to them,⁶ long-chain branches align to the backbone by the applied hydrodynamic force, and thus, the branch part is engaged in the same tube of the backbone. As a result, the branched polymer loses the

characteristics, such as high melt elasticity. Therefore, a polymer with more and/or longer long-branches exhibits “shear modification” significantly.^{4,12} In other words, there is a great possibility to evaluate the characteristics of long-chain branches, such as length and frequency, by quantitative analysis of “shear modification.”^{4,13} Rokudai suggested that the quantitative analysis of the effect of processing history on the swell ratio of extrudates and end-pressure-drop in a capillary flow gives the information on the characterization of long-chain branches in LDPE.⁴ Yamaguchi and Gogos have carried out quantitative characterization of the rheological change during the postprocessing annealing treatment above the melting point, i.e., the recovery process from “shear modified” state.¹³ According to their study employing a cone-and-plate rheometer as a “processing” device, the depression of melt elasticity was determined by the applied shear stress and the residence time at the processing.¹³ Further, Yamaguchi et al. also demonstrated that rheological properties and processability of low-density polyethylene (LDPE) were able to be controlled by the configuration of screw segment in an extruder.¹⁴ Their study revealed that relentless, high-stress flow field with less chaotic nature accelerates the depression of melt elasticity, i.e., alignment of long-chain branches.

Besides LDPE, it has been reported that ethylene-vinylacetate copolymer⁵ and polypropylene with long-chain branches, called “high-melt-strength PP,”¹⁵

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show "shear modification." Moreover, Maxwell et al. found that blends of LDPE with high-density polyethylene also show shear modification,⁸ in which the depression of elastic properties becomes more obvious with increasing LDPE content. This is reasonable since high-density polyethylene is a linear polymer whose rheological properties will not be basically affected by the processing and annealing history as long as neither molecular scission nor crosslink reactions occur.

Regarding the rheological properties of polyethylene blends, it has been clarified that some of them exhibit higher melt elasticity and zero shear viscosity than the individual pure components.¹⁷⁻²⁴ According to Wagner et al.,²³ the blends composed of LLDPE by Ziegler-Natta catalyst having higher viscosity and LDPE by autoclave process show more pronounced strain-hardening in elongational viscosity than the pure LDPE. Based on the quantitative characterization by the nonlinear constitutive equation proposed by Wagner et al.,^{25,26} called molecular stress function theory, it has been suggested that molecular aggregation state of the blend is heterogeneous; the matrix is composed of higher molecular weight fraction of LLDPE and LDPE with long-chain branches. The obtained result is similar to the work by Chen et al.,²⁷ in which they demonstrated the phase-separation between linear and highly branched amorphous polyolefins by neutron scattering. The rheological characterization performed in our preceding article²³ will be a useful technique to examine such type of conventional blends because any microscopic method does not work for the observation of phase-separated morphology by the following reasons: (1) the contrast between both phases is too weak even after staining because of the similar molecular structure and degree of crystallization and (2) a rapid crystallization, which may induce morphology change, prohibits the direct observation of the morphology in the molten state. Further, as shown in the previous article,²³ interfacial tension between the phases is too low to evaluate by means of emulsion model proposed by Paliarne,²⁸ although the characterization technique is applicable for a blend with fairly low interfacial tension, e.g., 0.3 mN/m, demonstrated by Yamaguchi and Miyata.²⁹ The difficulty of the morphology observation was also confirmed for LDPE/LLDPE blends as mentioned in our previous paper.²³ To the best of our knowledge, the shear modification behavior of such a "synergetic system" or "molecular composite" has not been studied yet in spite of the serious effect on the processability and thus the properties of the final product. In this article, we have studied the effect of blending LLDPE with higher viscosity to LDPE on the shear modification behavior, i.e., the phenomenon ascribed to long chain branches.

EXPERIMENTAL

Materials and processing history

The polymers employed in this study, such as linear low-density polyethylene produced by Ziegler-Natta catalyst (LLDPE) and low-density polyethylene by autoclave process (LDPE), were commercial materials that have already been investigated in previous works.²³ Number of long-chain branches (C_n with $n \geq 6$) evaluated by NMR was 5 per 1000 backbone carbon atoms. The LLDPE was a copolymer with 3.6 mol % of 1-butene produced by Ziegler-Natta catalyst. The molecular weights of both polymers are the followings: $M_n = 2.6 \times 10^4$, $M_w = 1.1 \times 10^5$ for LLDPE and $M_n = 2.6 \times 10^4$, $M_w = 2.1 \times 10^5$ for LDPE.

The mechanical processing history was applied for the samples, i.e., LDPE, LLDPE, and their blends, with small amount of thermal stabilizer by an internal batch mixer (Toyoseiki, Labo-Plastomil) at a rotor rate of 30 rpm at 130°C for 2 h. As demonstrated in the preceding article,¹³ the processing history does not affect the molecular weight and the number of long-chain branches. After taking out from the mixer, the material was compressed into a flat sheet and cooled down immediately. Furthermore, the processing history was also applied by a two-roll mill at 130°C for 15 min to characterize the rheological properties at an equilibrium state, such as oscillatory shear modulus, steady-state shear stress, and primary normal stress difference. According to the previous study,^{14,23} the molecular conformation of the sample processed by a two-roll mill is considered as the equilibrium state, and thus, the rheological properties are independent of the postprocessing annealing.

Measurements

The oscillatory shear modulus in the molten state was measured by a strain-controlled cone-and-plate rheometer (UBM, MR500) at 160°C under a nitrogen atmosphere. After setting the sample immediately between the cone and the plate, which were heated previously, we measured the oscillatory shear modulus at a constant frequency as a function of the residence time in the rheometer, i.e., the annealing time. The detail procedure was mentioned in the previous article.¹³

Further, rheological properties under steady-state shear flow and oscillatory shear modulus were also measured at 190°C by the rheometer.

RESULTS

Viscoelastic properties for the samples processed by two-roll mill

It has been reported that LDPE processed by a two-roll mill shows the same rheological properties as the sam-

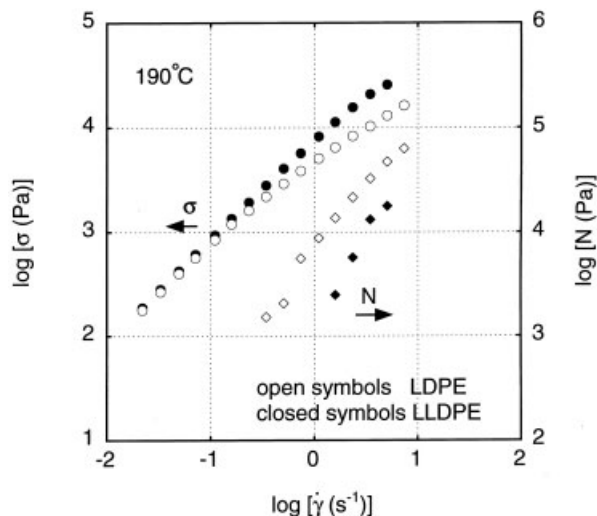


Figure 1 Shear rate $\dot{\gamma}$ dependence of steady-state shear stress, σ , (circles) and primary normal stress difference, N , (diamonds) at 190°C for LDPE (open symbols) and LLDPE (closed symbols).

ple treated by a solvent, suggesting that the molecular conformation state around branch point of the sample is thermodynamically stable.⁴ Therefore, the rheological properties are independent of the postprocessing annealing. Prior to the investigation of the mechanical modification, the rheological properties of the sample at the equilibrium state were studied.

Figure 1 shows the shear stress σ and the primary normal stress difference N at 190°C under the steady-state shear flow plotted against the applied shear rate $\dot{\gamma}$ for LDPE and LLDPE. Shear stress of both samples shows a similar level especially in the lower shear rate region, although LLDPE exhibits higher stress, i.e., viscosity, in the high shear rate region. This is reasonable because LDPE having long-chain branches as well as broad molecular weight distribution shows marked shear thinning behavior. As for the primary normal stress difference, however, LDPE shows higher values, i.e., higher melt elasticity.

Figure 2 illustrates the steady-state shear viscosity for the blends at various shear rates at 190°C. All samples show Newtonian behavior at the lowest shear rate, i.e., 0.022 s⁻¹. It is apparent that the blends show higher zero shear viscosity as discussed in the previous article.²³ Such kinds of rheological properties were observed for specific polyethylene blends, which could be called as “polyethylene molecular composites.”¹⁵ In our previous article, the enhanced rheological properties for polyethylene blends are observed when linear polyethylene shows higher viscosity than LDPE by autoclave process.^{15,23} As seen in the figure, LLDPE and LLDPE-rich blends show weak non-Newtonian behavior, i.e., poor shear-thinning.

For the purpose to obtain the information on the shear viscosity at higher shear rate, which has to be

considered when blending in a conventional mixer, the absolute value of complex shear viscosity η^* was plotted against the angular frequency ω at 130 and 190°C in Figure 3. Assuming the well-known Cox-Merz relation,³⁰ the figure represents the relation between shear viscosity and shear rate. In the higher frequency region, the order of the viscosity corresponds with that of the content of LLDPE at both temperatures, indicating that the applied stress in the mixer decreases with decreasing the content of LLDPE.

The growth curves of elongational viscosities and the drawdown force were also evaluated in the previous article.²³ It was founded that the blends with 20–60% of LLDPE show more pronounced strain-hardening than the pure LDPE. Moreover, the drawdown forces of the blends are higher than those of the individual pure components.

Recovery of oscillatory modulus in postprocessing annealing

Figure 4 shows the growth curves of oscillatory shear modulus as a function of the postprocessing annealing time in the cone-and-plate rheometer at 160°C at 0.01 Hz. Except for LLDPE, the processing history depresses the modulus, especially storage modulus G' , because of the suppression of long-time relaxation mechanism ascribed to the reptation of long-chain branches. Further, it was found that both moduli increase with the annealing time, which is owing to the recovery by micro-Brownian motion from the low enthalpy state around branch point. Furthermore, the depression and the recovery of modulus are less prominent at higher frequency region, although it is

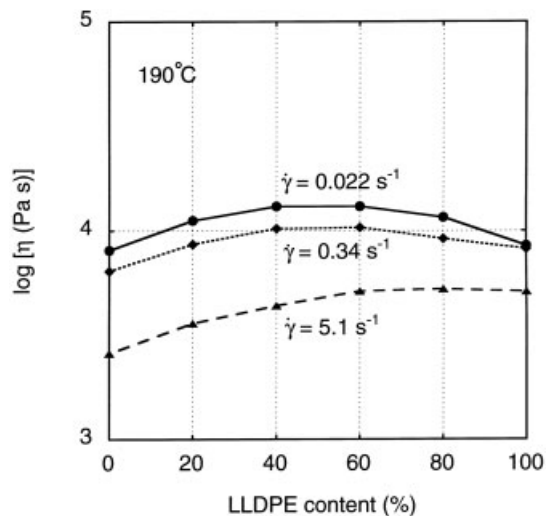


Figure 2 Shear viscosities at (●) $\dot{\gamma} = 0.022 \text{ s}^{-1}$, (◆) $\dot{\gamma} = 0.34 \text{ s}^{-1}$, and (▲) $\dot{\gamma} = 5.1 \text{ s}^{-1}$ at various blend ratios at 190°C.

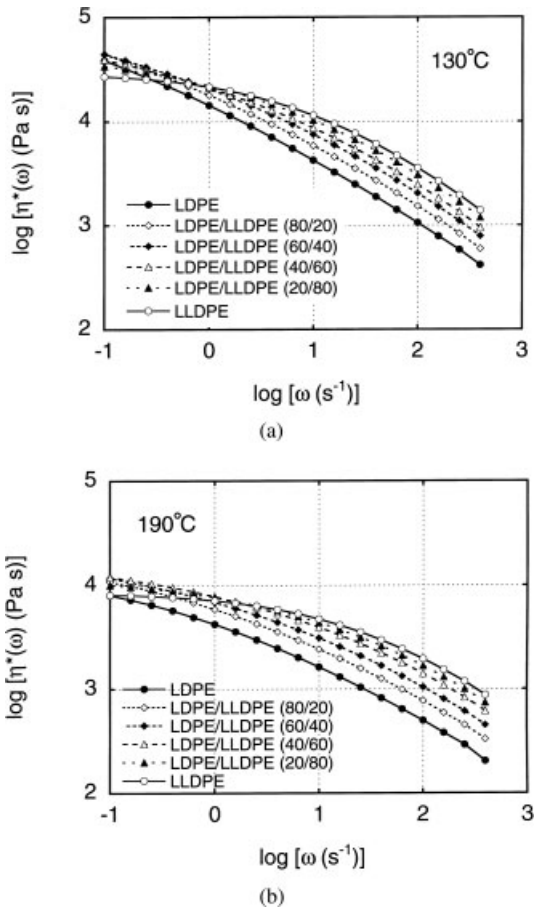


Figure 3 (a) Absolute value of complex shear viscosity $\eta^*(\omega)$ plotted against angular frequency ω at 130°C for (●) LDPE, (◇) LDPE/LLDPE (80/20), (◆) LDPE/LLDPE (60/40), (△) LDPE/LLDPE (40/60), (▲) LDPE/LLDPE (20/80), and (○) LLDPE. (b) Absolute value of complex shear viscosity $\eta^*(\omega)$ plotted against angular frequency ω at 190°C for (●) LDPE, (◇) LDPE/LLDPE (80/20), (◆) LDPE/LLDPE (60/40), (△) LDPE/LLDPE (40/60), (▲) LDPE/LLDPE (20/80), and (○) LLDPE.

not shown here, as reported in the previous article in detail.¹³

According to Yamaguchi and Gogos, the recovery curves of storage modulus are expressed by the following relation¹³:

$$G'(\omega, t) = G'_{\text{eq}}(\omega, t = \infty)[1 - \phi \exp(-t/\tau)] \quad (1)$$

where t the annealing time and G'_{eq} the storage modulus at an equilibrium state

The parameters ϕ and τ in eq. (1) would be determined by the molecular structure, especially associated with long-chain branches. More long-chain branches would reduce the initial modulus at $t = 0$, leading to large ϕ , whereas longer long branches would be responsible for the longer recovery time, i.e., large τ .

It is confirmed that the recovery curves of the blends as well as LDPE in this experiment are also expressed by eq. (1), which is written as follows:

$$\ln \left[1 - \frac{G'(\omega, t)}{G'_{\text{eq}}(\omega, t = \infty)} \right] = \ln \phi - \frac{t}{\tau} \quad (2)$$

The parameters ϕ and τ are evaluated by the plot of $\ln [1 - G'/G'_{\text{eq}}]$ versus t as shown in Figure 5. The figure demonstrates that the data can be expressed by one straight line for each sample. The inverse of the

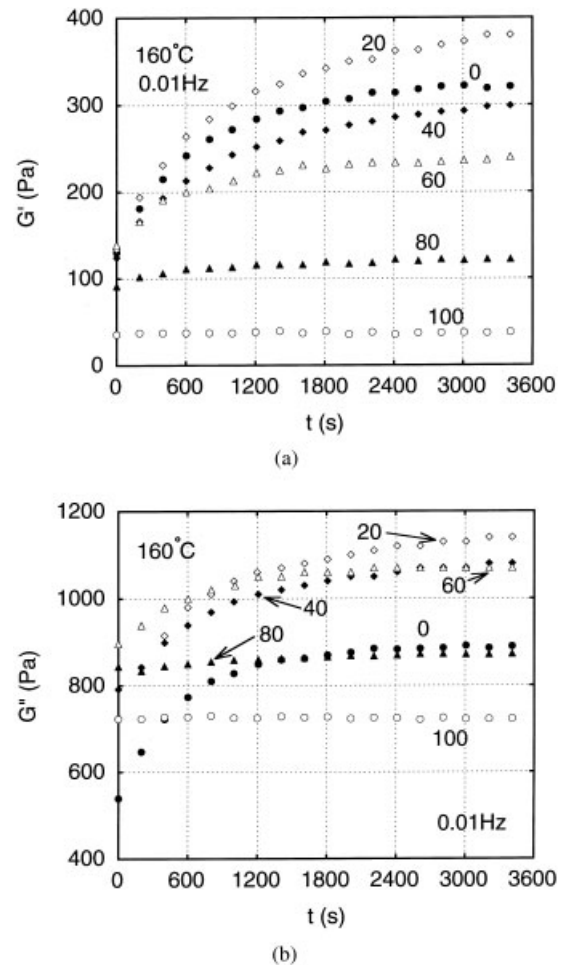


Figure 4 (a) Growth curves of shear storage modulus G' at 0.01 Hz plotted against the postprocessing annealing time t at 160°C for the sample processed by an internal mixer at 130°C for 2 h; (●) LDPE, (◇) LDPE/LLDPE (80/20), (◆) LDPE/LLDPE (60/40), (△) LDPE/LLDPE (40/60), (▲) LDPE/LLDPE (20/80), and (○) LLDPE. The numerals in the figure represent the weight fraction of LLDPE in LDPE/LLDPE blend. (b) Growth curves of shear loss modulus G'' at 0.01 Hz plotted against the postprocessing annealing time t at 160°C for the sample processed by an internal mixer at 130°C for 2 h; (●) LDPE, (◇) LDPE/LLDPE (80/20), (◆) LDPE/LLDPE (60/40), (△) LDPE/LLDPE (40/60), (▲) LDPE/LLDPE (20/80), and (○) LLDPE. The numerals in the figure represent the weight fraction of LLDPE in LDPE/LLDPE blend.

slope is τ , and ϕ is calculated from the value at $t = 0$. Figure 6 shows the parameters as a function of the blend ratio. It is clearly observed that LDPE/LLDPE (80/20) and (60/40) blends exhibit larger values than the pure LDPE, demonstrating that the rheological modification by the applied processing history for the blends is more prominent than that for the LDPE. The result supports that the blend system shows complicated molecular aggregation state, in which the matrix is composed of more long-chain branched polymer with high molecular weight as well as well-developed branch structure, although we have not yet succeeded the direct observation of the phase-separated morphology.

The concluded remark corresponds with anomalous rheological properties at an equilibrium state, such as strain-hardening in elongational viscosity and draw-down force, as shown in the previous article,²³ leading to the reduction of neck-in at T-die film-processing, the improvement of bubble stability at inflation film-processing, and the uniform wall-thickness of the products obtained by blow-molding or foaming. Moreover, this study emphasizes the importance of the control of mixing and processing procedures for such types of polyethylene blends with high melt elasticity.

CONCLUSIONS

The mechanical modification of rheological properties has been studied for anomalous polyethylene blend system, i.e., LDPE with a lot of long-chain branches produced by autoclave process and Ziegler-Natta LLDPE with higher viscosity. The applied processing history by an internal mixer de-

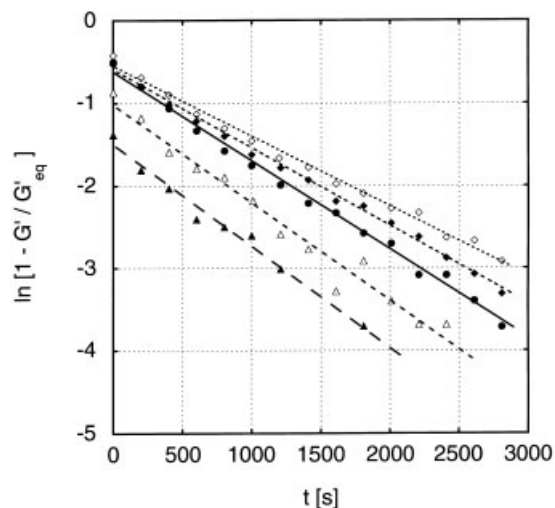


Figure 5 Annealing time t dependence of $\ln[G'(\omega, t)/G'_{eq}(\omega, t=\infty)]$ for (●) LDPE, (◇) LDPE/LLDPE (80/20), (◆) LDPE/LLDPE (60/40), (△) LDPE/LLDPE (40/60), and (▲) LDPE/LLDPE (20/80).

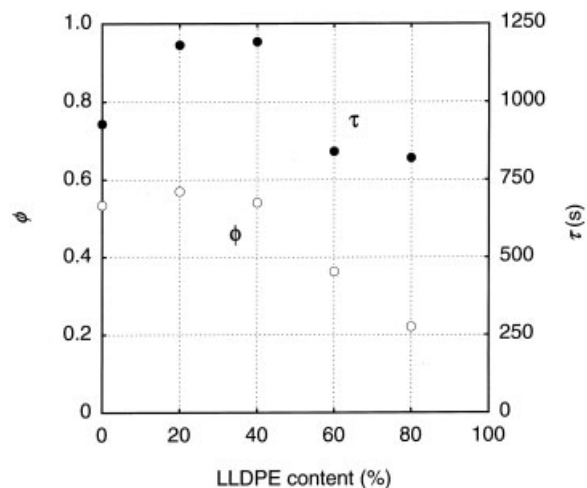


Figure 6 Relation between the parameters, ϕ and τ , and LLDPE content.

presses the elastic property to a great extent except for the pure LLDPE. Further, the postprocessing annealing above the melting point recovers the rheological properties to the original equilibrium state, which has been known as “shear modification.” Although the “shear modification” is believed to be specific feature for a branched polymer, the blends with 20–40 wt % of LLDPE show larger depression of storage modulus than the pure LDPE. Moreover, the blends show longer characteristic time for the recovery at the postprocessing annealing. The enhancement of “shear modification” behavior indicates that the molecular aggregation state of the blends is not homogeneous but microheterogeneous, in which higher molecular weight fraction with long-chain branches forms the matrix. The matrix would be responsible for the marked rheological modification by the processing and the postprocessing annealing procedures. The experimental results will be useful information when design a high-performance polyethylene blend with excellent mechanical properties and processability with high melt elasticity.

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