Enhanced Strain Hardening in Elongational Viscosity for HDPE/Crosslinked HDPE Blend. II. Processability of Thermoforming

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ABSTRACT: Rheological properties and processability of thermoforming were studied for high-density polyethylene (HDPE) and a blend of HDPE with crosslinked HDPE (xHDPE). Blending the xHDPE, which enhances melt strength and strain hardening in elongational viscosity of HDPE, helps the sheet avoid sagging in thermoforming. Moreover, the product of the blend obtained by vacuum forming has uniform wall thickness. Melt strength and strain hardening of the blend were, however, depressed by a processing history in a single-screw extruder, whereas reprocessing by a two-roll mill enhanced the melt strength again. It is considered that the processing history by a single-screw extruder, in which shear-dominant flow takes place, depresses the trapped entanglements between network chain of xHDPE and linear HDPE molecules, and results in low level of melt strength. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 79–83, 2002

Key words: polyethylene (PE); blends; rheology; gels; viscoelastic properties

INTRODUCTION

As demonstrated in the previous article,[1] melt strength, defined as the drawdown force needed for extension of a molten strand, and strain hardening in elongational viscosity of high-density polyethylene (HDPE) is greatly enhanced by blending crosslinked HDPE (xHDPE) having a high content of gel fraction with a low density of crosslink points, although steady-state shear viscosity and oscillatory shear modulus do not change drastically. In particular, significant enhancement is observed when the xHDPE is characterized as a critical gel at sol-gel transition from the viewpoints of mechanical properties. The origin of the anomalous rheological properties is considered to be chain stretching of network of the crosslinked polymer via trapped entanglements with linear molecules.[2–5]

Enhanced strain hardening in elongational viscosity is generally believed to be responsible for processability of various kinds of processing, such as blow molding, thermoforming, film inflation, spinning, and foaming.[3,6–9] Therefore, the crosslinked polymer is expected to be utilized as the modifier that improves processability of a linear polymer. Up to now, however, the processability of the blend with the crosslinked polymer has not been clarified except for foaming.[3]

In this study, we evaluated sagging behavior of molten material in thermoforming, which comes mainly from gravitational deformation of a flat sheet, and uniformity of wall thickness of the products obtained by vacuum forming for the blends composed of HDPE and xHDPE compared with the pure HDPE. Further, we associated the processability with the rheological properties to discuss the industrial application of the blend system, not only for thermoforming but also for blow molding. Another objective of this article is to clarify the effect of processing history on the rheological properties as well as the processability. The obtained results also gave us significantly important information to apply the blend system.

EXPERIMENTAL

Materials and blend preparation

Two kinds of high-density polyethylene (HDPE) [TOSOH Corporation, Nipolon Hard #5110, MFR = 0.95 g/10 min (HDPE1) and #8300A, MFR = 0.28 g/10 min (HDPE2)] were employed in this study. The number- and weight-average molecular weights are $M_n = 1.7 \times 10^4$ and $M_w = 1.0 \times 10^5$ for HDPE1, and $M_n = 1.1 \times 10^4$ and $M_w = 1.4 \times 10^5$ for HDPE2; HDPE2 has broader distribution of molecular weight.

The xHDPE used was crosslinked by 0.4 wt % of a peroxide compound, α,α'-bis(*tert*-butyl peroxy) diisopropyl benzene, in a compression mold at 190°C for 15 min, which was also employed in the previous article as s-xHDPE.[1] The preparation method and the char-

TABLE I
Temperature Profile of Sheet Extrusion

	C1	C2	C3	C4	H	D1	D2	D3
Set temperature (°C)	165	185	230	235	235	235	235	235

acteristics including mechanical properties of the xH-DPE have been discussed in detail.[1] HDPE1 and xH-DPE was mixed by a two-roll mill at 160°C for 10 min with 0.5 wt % of a thermal stabilizer. The blend ratio is 97/3 (HDPE/xHDPE, wt %). The obtained sheets were diced by a sheet pelletizer.

Measurements

Steady-state shear viscosity was measured at various shear rates using a cone-and-plate rheometer (Rheology, MR500) at 190°C under a nitrogen atmosphere.

Rheological properties in a capillary extrusion, such as extrudate swell ratio, melt strength, and ultimate draw ratio, were measured by a capillary rheometer (Toyoseiki, Capillograph) equipped with the capillary die employed in the previous study.[1] Temperature in the capillary reservoir cylinder and the die was kept at 160°C and the down speed of the plunger was 10 mm/min, yielding 10.8 s^{-1} of apparent shear rate. Swell ratio of extrudates was evaluated on-line by measuring the diameter of a molten strand using a laser beam. Further, the melt strength was examined by pulling a strand extruded vertically downward from the capillary rheometer at a rate of 10 m/min by a set of rotating wheels; this corresponds to a draw ratio of 47. Furthermore, the ultimate draw ratio, the draw ratio at break point of the strand, was also measured by increasing the pulling rate constantly. Measurements were carried out five times for each sample, and the average value was defined as the ultimate draw ratio.

Elongational viscosity was measured by a Meissner-type rheometer (Toyoseiki, Melten Rheometer) in a silicone oil bath at 160°C. Further, to calculate the
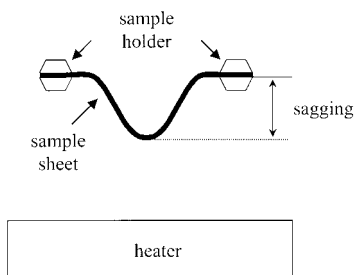

Figure 1 Measurement of sagging of a molten sheet. Bold line represents a sample sheet with 220 mm width and 320 mm length. Sagging level was measured as a function of heating time by a heater at 600°C.
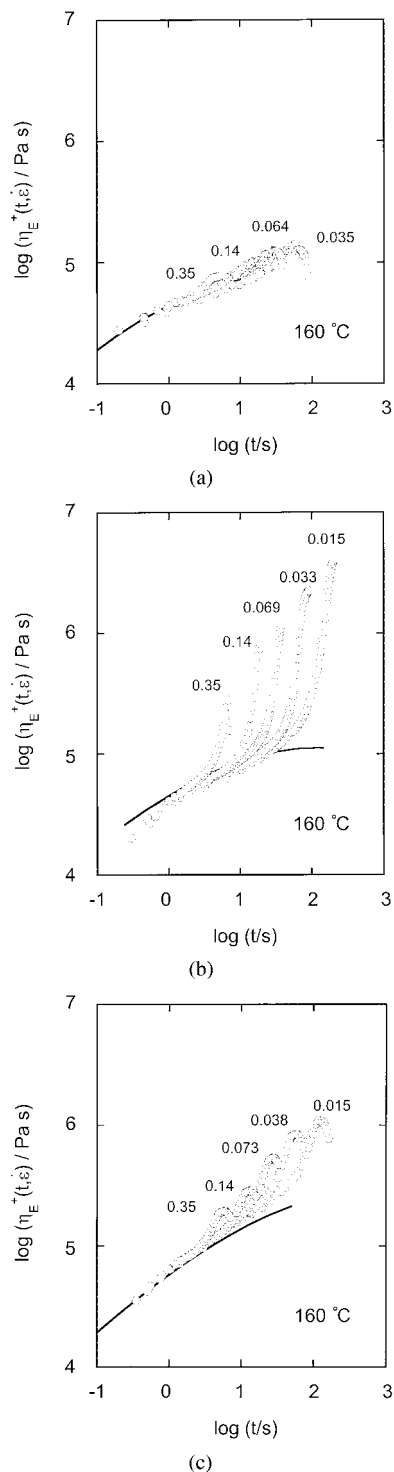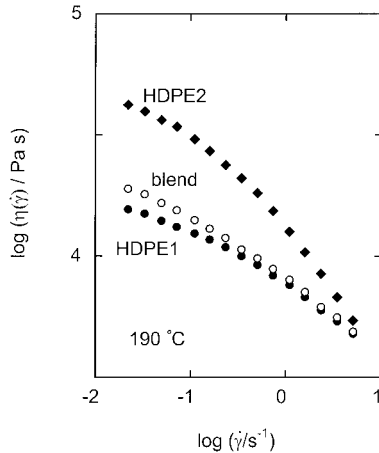

Figure 2 Growth curves of elongational viscosity η_E^+ $(t,\dot{\varepsilon})$ at 160°C for (a) HDPE1, (b) the blend, and (c) HDPE2. The numerals denote strain rates $\dot{\varepsilon}$, and the solid line represents $3\eta^+$ (t) where η (t) is the growth curve of shear viscosity at low strain rate asymptote calculated from oscillatory shear modulus.

growth curve of elongational viscosity at low strain rate asymptote, oscillatory shear modulus was measured by a cone-and-plate rheometer (Rheometrics,

Figure 3 Steady-state shear viscosity $\eta(\dot{\gamma})$ plotted against shear rate $\dot{\gamma}$ at 190°C for (●) HDPE1, (○) the blend, and (◆) HDPE2.

SR2000). Using the oscillatory shear modulus obtained, we predicted the growth curve of elongational viscosity in the linear viscoelastic region.

Processing

Sample sheets with 1.2-mm thickness were prepared by a 50 mm diameter single-screw extruder equipped with a coat-hunger die with 300 mm of the die-lip (Tanabe Plastics, VS50). Feed rate was around 14 kg/h, and the screw speed was 50 rpm. The temperature profile in the extruder was described in Table I. Further, the temperature of the cooling rolls was as follows: first roll 60°C, and second roll 80°C.

Sagging of a molten sheet, illustrated in Figure 1, was measured using a laboratory thermoforming machine (Asano, laboratory thermoforming machine) as a function of heating time. The dimension of the sample holder was 220 mm width and 320 mm length. The heater temperature was 600°C. A preheated sheet was vacuum formed directly onto the cup-mold, which was cooled down by chilled water at 30°C. The diameter of top of the cup is 100 mm and the depth is 65 mm. The heating time before vacuuming was 39 s. The wall thickness of the obtained cups was measured at 10 points along circumference of the cup 55 mm below the top. The degree of uniformity was evaluated using the following parameter U;

$$U = \frac{T_{\max} - T_{\min}}{T_{\text{ave}}} \tag{1}$$

where $T_{\max}$, $T_{\min}$, and T_{ave} are maximum, minimum, and average thickness. The measurements were carried out for 10 products and the average U, $\bar{U}$, was calculated.
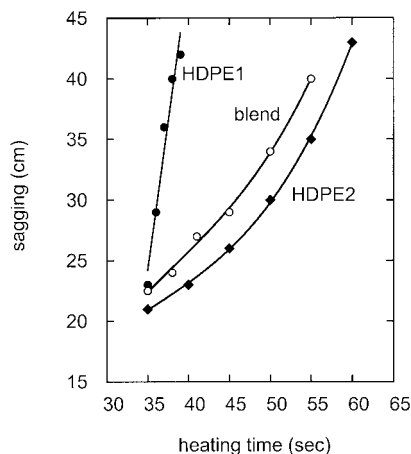
RESULTS AND DISCUSSION

Rheological properties

Figure 2 shows growth curves of uniaxial elongational viscosity η_E^+ $(t,\dot{\varepsilon})$ for HDPE1 [Fig. 2(a)], the blend [HDPE1/xHDPE (97/3, wt %)] [Fig. 2(b)], and HDPE2 [Fig. 2(c)] at various strain rates $\dot{\varepsilon}$ at 160°C. The solid lines in the figure represent the low strain rate asymptote calculated from oscillatory shear modulus in linear viscoelastic region.[10] As seen in the figure, HDPE1, having narrow molecular weight distribution, shows slight strain hardening behavior, whereas HDPE2 shows a larger strain hardening than HDPE1, because HDPE2 has a broader molecular weight distribution, i.e., a broader distribution of relaxation time. This result corresponds with the study carried out by Linster and Meissner using various HDPE having different molecular weight distributions.[11] Further, it was found that the blend exhibits marked strain hardening. The maximum value of elongational viscosity of the blend is considerably larger than that of HDPE2, suggesting that the blending of xHDPE is more effective to enhance the strain hardening in elongational viscosity than broadening the molecular weight distribution.

Figure 3 shows steady-state shear viscosity $\eta(\dot{\gamma})$ at 190°C plotted against shear rates $\dot{\gamma}$. The blend shows somewhat larger shear viscosity than the pure HDPE1. On the other hand, HDPE2 exhibits a high shear viscosity, especially in the lower shear rate region because of the broad distribution of the relaxation time.

Capillary extrusion properties, such as melt flow rate (MFR) at 190°C, extrudate swell, melt strength, and ultimate draw ratio, were also measured, and the results were summarized in Table II. As seen in the table, MFR of the blend is lower than that of the pure HDPE1, although shear viscosity is almost similar to that of HDPE1. This is attributed to the difference in

TABLE II
Rheological Parameters in Capillary Extrusion

	HDPE1	HDPE1/xHDPE	HDPE2
MFR	0.95	0.60	0.28
Melt strength (mN)	75	430	150
Extrudate swell ratio	1.42	1.80	1.51
Ultimate draw ratio	255	40	155

Figure 4 Sagging level plotted against heating time for (●) HDPE1, (○) the blend, and (◆) HDPE2.

TABLE III
Uniformity of Wall Thickness

	HDPE1	HDPE1/xHDPE	HDPE2
$\bar{U}$	0.349	0.313	0.310

the non-zero pressure at capillary exit because of the high melt elasticity of the blend, which is enhanced for a short-length die, such as that used at the MFR measurement. It is also found that the order of melt strength agrees well with the maximum value of elongational viscosity in Figure 2. Further, the table shows that a high level of melt strength of the blend results in less drawability. This is reasonable because high stress leads to a brittle rupture. Moreover, the blend exhibits a large value of extrudate swell, which comes from pronounced primary normal stress difference.

Processability

Processability of thermoforming, especially, vacuum forming, was investigated considering the relationship with the rheological properties. During vacuum forming including the heating step, elongational flow has to be taken into account[12] instead of shear flow, because drag flow does not take place. Therefore, sagging level and uniformity of wall thickness, which are important properties for thermoforming as well as blow molding, were discussed in terms of elongational viscosity shown in Figure 2.

Sagging behavior by gravitational force was studied using the sample sheet produced by a single-screw extruder equipped with a coat-hunger die. Figure 4 shows the result of the sagging level plotted against the heating time. In this experiment, all sample sheets were molten around 22 s and then drawn down gradually with heating time. As seen in the figure, sagging level increases rapidly with heating time for HDPE1 because of the low elongational viscosity. On the other hand, the blend exhibits lower level of sagging than HDPE1 at the same heating time, demonstrating that the blend has broader operating condition at thermoforming. Further, HDPE2 exhibits a lower level of sagging than the blend, although the level of maxi-

mum value of the elongational viscosity is less than that of the blend, as shown in Figure 2.

Uniformity of the wall thickness of the products was also evaluated. As is summarized in Table III, the wall thickness of the blend and HDPE2 is more uniform than that of HDPE1. This is reasonable because HDPE1 sagged before vacuum forming more than HDPE2 and the blend, as shown in Figure 4. Furthermore, enhanced strain hardening in elongational viscosity will lead to homogeneous deformation during forming.

For the better understanding of sagging and wall thickness of the products, elongational viscosity of the sheet sample produced by the single-screw extruder was measured after preparing rod-shaped samples by the capillary rheometer. Figure 5 shows the growth curves of elongational viscosity for the blend with the processing history by the single-screw extruder. Apparently, the strain hardening is less than that in Figure 2(b), although the elongational viscosity in linear region, i.e., prior to strain hardening, is the same as those in Figure 2(a) and (b). This suggests that linear viscoelastic properties, such as oscillatory shear modulus, are not affected considerably by the processing history. Further, we confirmed, but not presented here, that elongational viscosity of HDPE1 and HDPE2 was not changed by the processing. The origin of the depressed strain hardening in elongational viscosity of the blend is attributed to disentanglements
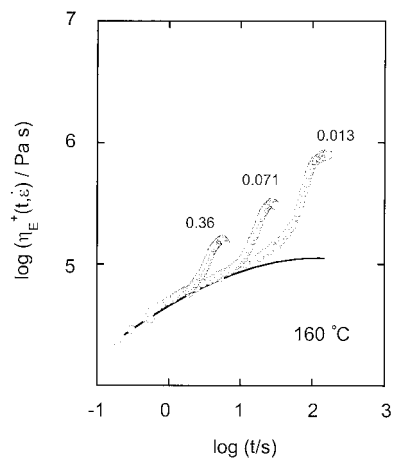
Figure 5 Growth curves of elongational viscosity η_E^+ $(t,\dot{\varepsilon})$ at 160°C for the blend processed by a single-screw extruder. The numerals denote strain rates $\dot{\varepsilon}$, and the solid line represents $3\eta^+$ (t), where η^+ (t) is the growth curve of shear viscosity at a low strain rate asymptote calculated from the oscillatory shear modulus.

TABLE IV
Effect of Processing History on Melt Strength (mN)

	HDPE1	HDPE1/xHDPE	HDPE2
Before sheet forming	75	430	150
After sheet forming	75	140	150
After reprocessing by two-roll mill	75	420	150

between network chain of xHDPE and linear molecules of HDPE because of shear-dominated flow in the single-screw extruder. A decrease in the interaction between xHDPE and HDPE, i.e., a decrease in the density of trapped entanglements, leads to depressed stretching of the network chain in xHDPE under elongational flow at a constant strain rate, which is the origin of the decrease in the strain hardening.

Furthermore, it is found that the blend exhibits high melt strength again after reprocessing by the two-roll mill. Table IV summarizes the melt strength of the samples with various processing histories. Reprocessing by the two-roll mill was carried out at the same condition as mixing. As seen in the table, melt strength of HDPE1 and HDPE2 do not change by the processing history. On the other hand, melt strength of the blend is quite dependent on the processing history. The result indicates that a two-roll mill processing, in which elongational deformation takes place dominantly, enhances the interaction between network chain and linear molecules. Further analysis of the flow in the two-roll mill, which also affects the rheological properties of LDPE to a great degree,[13] will be discussed in detail.[14]

These results demonstrate that the processing history and processing method have to be considered seriously when the blend with the crosslinked polymer is used for an industrial application. Further investigation on the effect of processing history on morphology and rheological properties of the blend system is being carried out currently compared with "shear modification" of LDPE.[14]

CONCLUSION

Blending a small amount of crosslinked HDPE enhances melt strength and strain hardening in elongational viscosity of HDPE to a great degree, although it has little effect on steady-state shear viscosity. This pronounced strain hardening is responsible for improvement of the sagging level of a molten sheet in thermoforming, which extends the processing condition. Furthermore, it is also responsible for uniform wall thickness of the products. This is owing to less sagging level before vacuum forming and pronounced strain hardening in elongational viscosity, which leads to homogeneous deformation during forming. However, processing history in a single-screw extruder depresses the melt strength and the strain hardening, and results in a high level of sagging. Reprocessing in a two-roll mill enhances the melt strength again, demonstrating that processing history has to be seriously considered in case of the blend system.

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