

# Enhanced Strain Hardening in Elongational Viscosity for HDPE/Crosslinked HDPE Blend. I. Characteristics of Crosslinked HDPE

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**ABSTRACT:** Blending a crosslinked high-density polyethylene (xHDPE) enhances melt strength and strain hardening behavior in elongational viscosity of high-density polyethylene (HDPE) to a great degree. Gel fraction of xHDPE has a stronger effect on the strain hardening than sol fraction, although sol fraction also enhances the strain hardening to some degree. Further, the xHDPE crosslinked by peroxide in a compression mold exhibits more pronounced effect than xHDPE by radiation, which is attributed to the difference in the amount of the gel frac-

tion. The xHDPE, which enhances the strain hardening, has sparse crosslink points in the network. Moreover, it was found from linear viscoelastic measurements, such as oscillatory modulus and relaxation modulus, that the xHDPE is characterized as a critical gel, which was also supported by the result of tensile testing. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 73–78, 2002

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

## INTRODUCTION

It has been generally accepted that strain hardening behavior in elongational viscosity, which is defined as an upturn departure of elongational viscosity from the low strain rate asymptote, is responsible for processability of various kinds of processing. Therefore, considerable effort has been paid to enhance the strain-hardening behavior, as summarized in our previous paper.<sup>1</sup> According to our recent studies,<sup>1–3</sup> a small amount of a crosslinked polymer enhances the strain hardening in elongational viscosity of a linear polymer, when the following conditions are satisfied: (1) the crosslinked polymer has a network chain with a low density of crosslink points; (2) the precursor of the crosslinked polymer is miscible with the linear polymer. Moreover, melt elasticity, such as extrudate swell, is also enhanced by blending the crosslinked polymer, although the blend shows a similar steady-state shear viscosity as the linear polymer. The origin of the anomalous rheological properties is believed to be chain stretching of network polymers via trapped entanglements with a linear polymer.<sup>2,3</sup>

From an industrial point of view, the crosslinked polymer will be applicable as a modifier of processing, because most linear polymers having less melt elastic-

ity and less strain hardening in elongational viscosity will become available for various kinds of processing by employing the blend technique. For example, a crosslinked high-density polyethylenes (xHDPE) will be available for a processing modifier of HDPE having no long chain branches, as is discussed in this article. It is well known that there are many ways to produce crosslinked HDPE, such as peroxide modification and radiation modification. However, it has not been clarified what kinds of xHDPE has a marked effect on the enhancement of elongational viscosity, because detail characteristics of the crosslinked polymer have not been investigated in the previous articles.<sup>1–3</sup>

The objectives of this study are as follows: (1) to establish the production method of the xHDPE, which leads to enhance of the strain hardening in elongational viscosity of HDPE. The discussion has been carried out based upon the rheological properties, such as melt strength and elongational viscosity, of the blends composed of HDPE and various kinds of xHDPEs; (2) to clarify the detailed characteristics of the xHDPE by means of solvent extraction measurements, dynamic mechanical measurements, stress-relaxation measurements, and tensile testing.

## EXPERIMENTAL

### Materials and blend preparation

High-density polyethylene (HDPE) used was a commercial material (TOSOH Corporation, Nipolon Hard #5110). The number- and weight-average molecular

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weights, determined by gel permeation chromatography (Waters, 150-C) at 135°C using *ortho*-dichlorobenzene as a solvent, are  $M_n = 1.7 \times 10^4$  and  $M_w = 1.0 \times 10^5$ .

Various xHDPEs were prepared by peroxide modification as follows. After mixing with various amounts of a peroxide compound,  $\alpha, \alpha'$ -bis(*tert*-butyl peroxy) diisopropyl benzene, in an 8-inch two-roll mill on which surface temperature was kept at 150°C, the obtained compound was crosslinked either (1) in a compression-mold at 190°C for 15 min, s-xHDPE; or (2) in an internal batch mixer (Toyoseiki, Labo-Plasto-mill) during kneading at 30 rpm at 190°C for 15 min, d-xHDPE. Further, xHDPEs were also prepared by radiation, r-xHDPE. The plates of the HDPE, with 1-mm thickness, prepared by compression molding, were irradiated at room temperature under a nitrogen atmosphere. Moreover, in an attempt to clarify the role of gel and sol fractions on the rheological properties of the blend, 1 wt % solution of d-xHDPE crosslinked by 0.6 wt % of the peroxide in 1,2,4-trichlorobenzene was centrifuged at 120°C at 12,000 rpm for 1 h (Kokusan, H-175). After centrifuging, the precipitation, gel-rich fraction, and the solution, sol-rich fraction, were separated, washed by methanol, and dried.

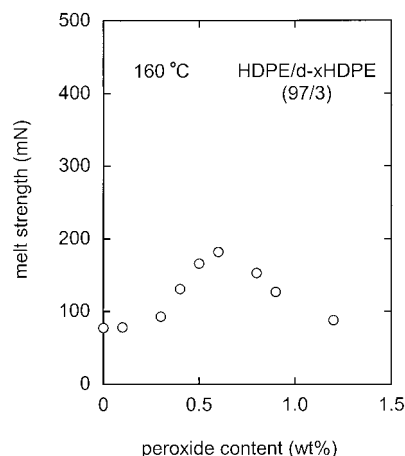
Mixing of HDPE with xHDPE was carried out mechanically by the two-roll mill at 160°C for 10 min with 0.5 wt % of a thermal stabilizer, 2,6-di-*tert*-butyl *para*-cresol. The rotating speed was 20 rpm for the front roll and 24 rpm for the rear. The obtained sheets were formed into flat plates by compression molding at 190°C and at 10 MPa for 15 min for measurements of the rheological properties.

## Measurements

Gel fraction of xHDPE was measured by solvent extraction method using *para*-xylene as a solvent. Furthermore, following Flory-Rhener equation,<sup>4</sup> average molecular weight between crosslink points,  $M_c$ , of gel fraction of xHDPE was calculated. The details were described in ref. 5.

Frequency dependence of oscillatory shear moduli for the xHDPE was measured using a parallel-plate rheometer (Rheology, MR500) at 190°C. Further, relaxation modulus was also measured by the rheometer at 190°C. The applied shear strain was 0.4. Both measurements were carried out under a nitrogen atmosphere to avoid thermo-oxidative degradation.

Melt strength, defined as the drawdown force needed for stretching of a strand, was measured at 160°C using a capillary rheometer (Toyoseiki, Capilograph) equipped with a capillary die having an 8 mm length and 2.095 mm diameter, and an entrance angle of  $\pi/2$ . The force was measured by pulling the extruded strand from the capillary rheometer by a set of winding rolls at a rate of 10 m/min. Temperature in



**Figure 1** Melt strength of HDPE/d-xHDPE (97/3) blends at 160°C plotted against peroxide content (wt %) in d-xHDPE.

the capillary reservoir cylinder and the die was kept at 160°C, and the down speed of the plunger was 10 mm/min, yielding a 47 stretching ratio.

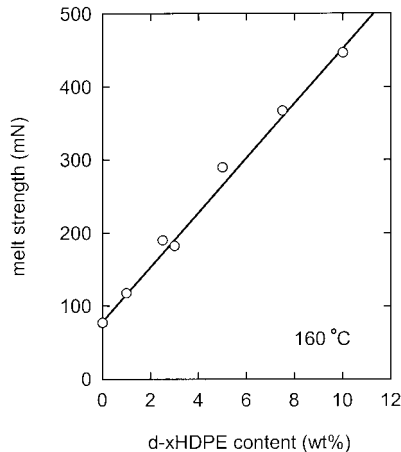
Growth curve of uniaxial elongational viscosity was measured in a silicone oil bath at 160°C using a Meissner-type rheometer (Toyoseiki, MELTEN Rheometer) at various strain rates. Rod-like samples with a diameter of 3–4 mm and length 150–170 mm were prepared by means of the capillary rheometer at 160°C. It was confirmed by a video camera that homogeneous deformation takes place during stretching for all samples.

Tensile testing of xHDPE was carried out using a dynamic mechanical analyzer (Rheology, DVE-V4), which was improved to have the capability of subjecting a specimen to elongate at a constant stretching rate. The following conditions were employed: temperature 190°C, initial length between upper and lower clamps of 20 mm, and stretching rate of 1.0 mm/min. The stress was calculated by dividing the tensile load by the initial cross-sectional area, and the strain was evaluated from the ratio of the increment of the length between clamps to initial length.

## RESULTS AND DISCUSSION

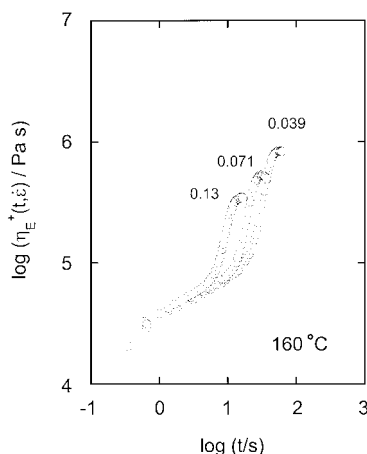
### Rheological properties of HDPE/xHDPE blend

Figure 1 shows the melt strength of the blends with 3 wt % of d-xHDPE, the xHDPE crosslinked by peroxide in an internal batch mixer during kneading. As seen in the figure, the d-xHDPE crosslinked by 0.6 wt % of the peroxide has the most significant effect on the melt strength. Further, the melt strength increases with the amount of the xHDPE linearly, as shown in Figure 2. The melt strength of the blend with 3 wt % of the d-xHDPE exhibits twice as much as that of the pure HDPE.

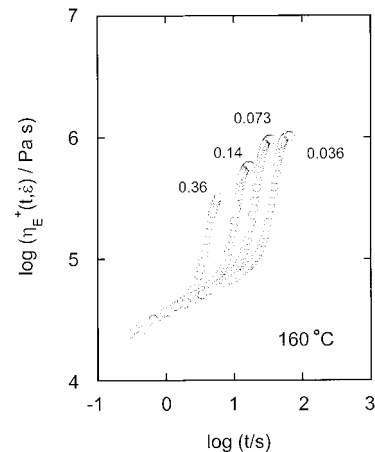


**Figure 2** Relation between d-xHDPE content (wt %) in the blend and melt strength at 160°C. The d-xHDPE employed was crosslinked by 0.6 wt % of the peroxide in an internal batch mixer during kneading.

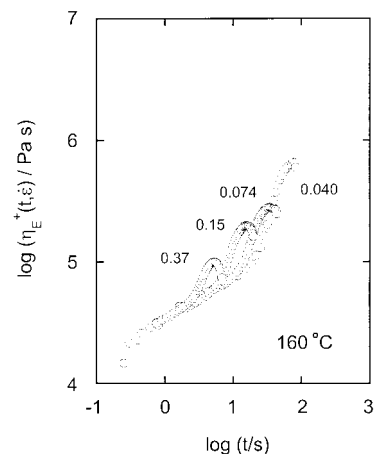
Figure 3 shows growth curves of elongational viscosity  $\eta_E^+(t, \dot{\epsilon})$  at various strain rates  $\dot{\epsilon}$  for the blend with the d-xHDPE crosslinked by 0.6 wt % of the peroxide. The blend ratio is 97/3 (w/w). As seen in the figure, elongational viscosity at low strain region, which is represented by a single curve irrespective of strain rates, shows a similar value as that of the pure HDPE. Elongational viscosity of the blend, however, increases rapidly at a high strain region at any strain rate. This result demonstrates that the high level of melt strength is ascribed to the enhanced strain hardening in elongational viscosity. Furthermore, the effect of gel and sol fractions in the d-xHDPE on the elongational viscosity of the blend was also studied using both fractions obtained by the centrifugal. Figure 4 shows growth curves of elongational viscosity for the



**Figure 3** Growth curves of elongational viscosity  $\eta_E^+(t, \dot{\epsilon})$  of HDPE/d-xHDPE (97/3) blend at various strain rates  $\dot{\epsilon}$  at 160°C. The numerals in the figure represent strain rate. The d-xHDPE was crosslinked by 0.6 wt % of the peroxide in an internal batch mixer during kneading.



(a)

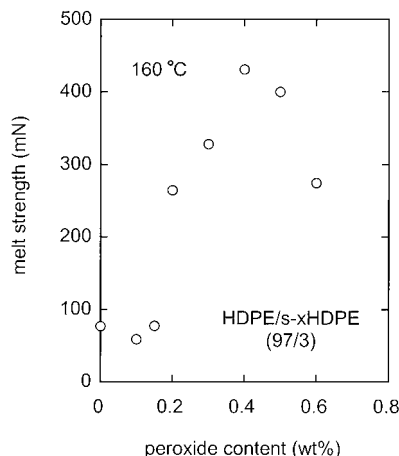


(b)

**Figure 4** Growth curves of elongational viscosity  $\eta_E^+(t, \dot{\epsilon})$  of the blends composed of 97 wt % of HDPE and 3 wt % of (a) gel fraction, and (b) sol fraction of the d-xHDPE at various strain rates  $\dot{\epsilon}$  at 160°C. The numerals in the figure represent strain rate. The d-xHDPE was crosslinked by 0.6 wt % of peroxide in an internal batch mixer during kneading.

blends with (a) gel-rich fraction and (b) sol-rich fraction in the d-xHDPE. As seen in the figure, it is found that the gel fraction is more responsible for the strain hardening, although sol fraction also enhances the strain hardening to some degree.

Melt strength of the blends with 3 wt % of s-xHDPE, the xHDPE crosslinked in a compression mold, is shown in Figure 5. The s-xHDPE crosslinked by 0.4 wt % of the peroxide has the strongest effect on the melt strength. Further, s-xHDPEs crosslinked by more than 0.6 wt % of the peroxide were not well dispersed in the HDPE. Consequently, the strand of the blend extruded by the capillary rheometer cannot be stretched enough because of brittle rupture at the vicinity of the large grain of the s-xHDPE. Moreover, compared to Figure 1, it is obvious that s-xHDPEs enhance melt strength of HDPE more than d-xHDPEs.



**Figure 5** Melt strength of HDPE/s-xHDPE (97/3) blends at 160°C plotted against peroxide content (wt %) in s-xHDPE.

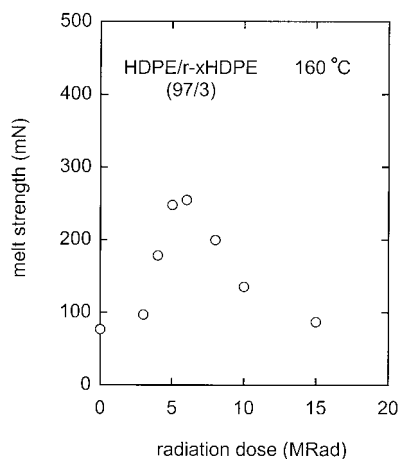
The effect of r-xHDPE, the HDPE crosslinked by radiation, was also investigated. Figure 6 shows the melt strength of the blends with 3 wt % of r-xHDPE. As seen in the figure, 5–6 MRad of radiation produces the r-xHDPEs that enhance melt strength. The level of melt strength is, however, lower than that for the blends with s-xHDPE.

As shown in Figures 1, 5, and 6, various xHDPEs enhance the melt strength of HDPE, when the amount of peroxide or radiation dose is appropriate. Furthermore, the level of melt strength considerably depends on the species of xHDPE. The xHDPE prepared by the peroxide in a compression mold has pronounced effect on melt strength of HDPE. On the other hand, the xHDPEs crosslinked by peroxide during kneading or by radiation show less effect on melt strength.

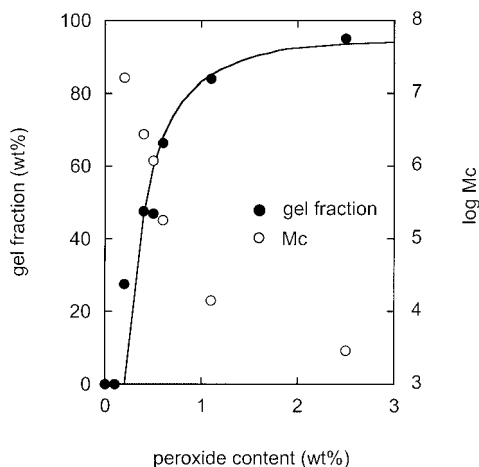
### Characteristics of s-xHDPE

#### Gel fraction and $M_c$

Figure 7 shows gel fraction of s-xHDPE. It is found that the gel fraction, which is more responsible for the



**Figure 6** Melt strength of HDPE/r-xHDPE (97/3) blends at 160°C plotted against radiation dose (MRad).



**Figure 7** Gel fraction of s-xHDPE and average molecular weight between crosslink points  $M_c$  of gel fraction of s-xHDPE. The solid line denotes the prediction following the theory developed by Charlesby and Pinner.

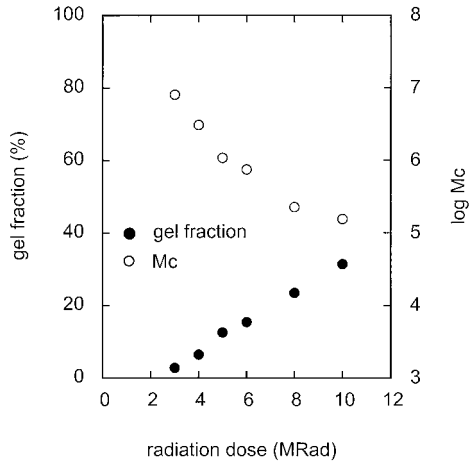
melt strength than the sol fraction, as shown in Figure 4, is well expressed by the Charlesby-Pinner equation, which was originally proposed for crosslinking by radiation as follows,<sup>6,7</sup>

$$s + s^{1/2} = A + B/[I] \quad (1)$$

where  $s$  is the sol fraction,  $[I]$  is the radiation dose, and  $A$  and  $B$  are the constants. The solid line in Figure 7 represents the theoretical prediction by eq. (1) using peroxide content instead of radiation dose.

Further, the  $M_c$  of the gel fraction of s-xHDPE, which is calculated by swelling ratio, decreases monotonically with peroxide content. As shown in Figure 5, the s-xHDPE crosslinked by 0.3–0.5 wt % of peroxide exhibits a marked effect on melt strength. Accordingly,  $M_c$  must be more than  $10^5$  to enhance the melt strength, because the s-xHDPE by 0.6 wt % of peroxide has less effect even though it has more gel fraction than the s-xHDPE by 0.5 wt %. According to our recent studies on peroxide-crosslinked polyethylenes,<sup>14</sup> the gel fraction rapidly increases with peroxide content when molecular weight distribution of the precursor is narrow. For example, the crosslinked polyethylene, whose precursor, a metallocene polyethylene, has narrow molecular weight distribution, has 75 wt % of gel fraction, although the  $M_c$  is over  $3.0 \times 10^5$ . Consequently, the crosslinked polyethylene exhibits pronounced effect on strain hardening in elongational viscosity. These results indicate that a polyethylene with narrow molecular weight distribution is preferred for the preparation of xHDPE as a modifier of rheological properties of HDPE.

Figure 8 shows the gel fraction and the  $M_c$  of the r-xHDPE plotted against the radiation dose. Compared to Figure 7, the gel fraction is quite less than that



**Figure 8** Gel fraction of r-xHDPE and average molecular weight between crosslink points  $M_c$  of the gel fraction of r-xHDPE.

of the s-xHDPE, when the  $M_c$  is larger than  $10^5$ . From the experimental results, it is concluded that the ability of the enhancement of melt strength depends on the production method of xHDPE, which decides the gel fraction as well as the density of crosslink points.

#### Oscillatory shear modulus

Figure 9 shows frequency dependence of storage shear modulus  $G'$  [Fig. 9(a)] and  $\tan \delta$  [Fig. 9(b)] at  $190^\circ\text{C}$  for s-xHDPEs with various amounts of the peroxide. It is found that storage modulus monotonically increases and  $\tan \delta$  decreases with the amount of peroxide. Further,  $\tan \delta$  remains a constant value irrespective of frequencies, when the peroxide content is below 0.6 wt %. According to Valles et al.,<sup>8-11</sup> linear viscoelastic properties, such as oscillatory modulus and relaxation modulus  $G(t)$ , of radiation crosslinked HDPE in wider vicinity of gel point are governed by the following scaling law:

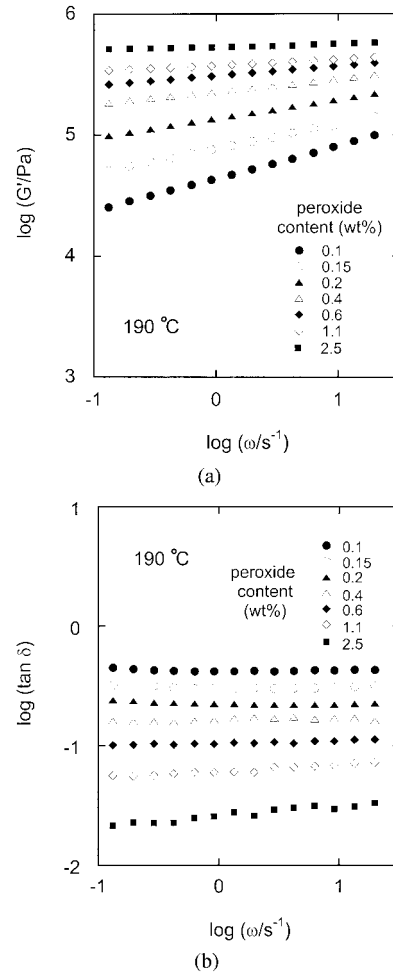
$$G' \propto G'' \propto \omega^n \quad (2)$$

$$\tan \delta = \tan\left(\frac{n\pi}{2}\right) \quad (3)$$

$$G(t) = St^{-n} \quad (4)$$

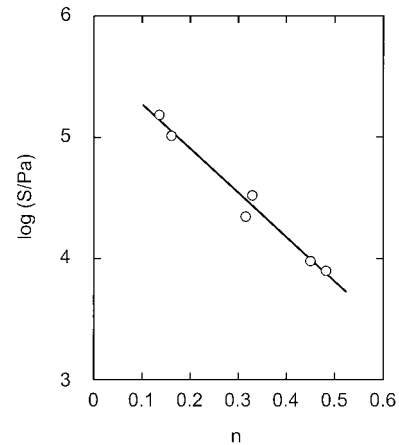
where  $S$  is the gel strength.

In this experiment, we also confirmed that  $G(t)$  obeys eq. (4), although they are not presented here. According to the results, gel strength  $S$  of the s-xHDPE crosslinked by 0.4 wt % of the peroxide, which enhances melt strength to a great degree, is found to be 0.33 MPa. Further,  $n$  is evaluated to be 0.33, which well agrees with the value estimated from  $\tan \delta$  in Figure



**Figure 9** Frequency dependence of (a) storage shear modulus  $G'$  and (b)  $\tan \delta$  at  $190^\circ\text{C}$  of s-xHDPEs with various peroxide contents. The numerals in the figure represent peroxide content (wt %).

9(b). Figure 10 shows the relation of  $n$  and  $S$  for various s-xHDPEs. According to Valles et al.,<sup>8</sup>  $S$  is expressed by the following relation:



**Figure 10** Plots of scaling parameter  $n$  and gel strength  $S$  for the s-xHDPE crosslinked by 0.1–0.6 wt % of the peroxide.



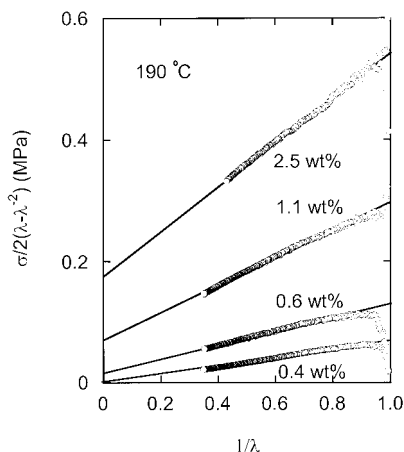


Figure 11 Mooney-Rivlin plots for s-xHDPE at 190°C.

$$S = G_0 \tau_0^n \quad (5)$$

where  $\tau_0$  is the characteristic shortest relation time and  $G_0$  is the characteristic modulus.

As shown in Figure 10, our experimental results are also in accordance with eq. (5). Moreover, the magnitude of  $G_0$ ,  $4.2 \times 10^5$  Pa, well agrees with that for the radiation-crosslinked HDPE.<sup>8</sup> This suggests that the smallest structure, where scaling rule is applicable, of the peroxide-crosslinked polyethylene is the same as that of the radiation-crosslinked polyethylene.

### Tensile testing

Stress-strain measurements were carried out at 190°C for the s-xHDPE, in which peroxide content is above 0.4 wt %, because the s-xHDPEs having less/no gel fraction do not give enough stress to measure. It is well known that stress-strain curves of most rubbers follow the Mooney-Rivlin equation:

$$\sigma = \left( 2c_1 + \frac{2c_2}{\lambda} \right) \left( \lambda - \frac{1}{\lambda^2} \right) \quad (6)$$

where  $\sigma$  the nominal stress,  $\lambda$  the extension ratio, and  $c_1$  and  $c_2$  the constants. It is generally accepted that both trapped entanglements and crosslink points contribute to  $c_1$ , whereas  $c_2$  is associated with trapped entanglements only.<sup>12-14</sup>

In Figure 11,  $\sigma/2(\lambda - \lambda^{-2})$  is plotted against  $\lambda^{-1}$ . In the experimental strain region, one straight line is obtained for each sample. The solid lines are extrapolated from experimental values denoted by the open circles. Moreover, it is found that both  $c_1$ ,  $y$ -intercept,

and  $c_2$ , the slope, increase with peroxide contents, i.e., gel fraction and  $M_c$ . The value of  $c_1$  of the s-xHDPE by 0.4 wt % of the peroxide is close to 0, indicating that most tensile stress is originated from trapped entanglements for the sample. This result also demonstrates that the s-xHDPE, which enhances melt strength to a great degree, is close to the sol-gel transition point.

### CONCLUSION

The characteristics of crosslinked high-density polyethylene (xHDPE) obtained by peroxide and radiation modification were studied to clarify the relation between structure of xHDPE and the ability to enhance the melt strength and strain hardening in elongational viscosity of HDPE. The peroxide-modified xHDPE crosslinked in a compression mold has stronger effect than radiation-crosslinked xHDPE, which is owing to a large amount of gel fraction in the peroxide-crosslinked xHDPE. Moreover, the peroxide-modified xHDPE crosslinked during kneading has less effect on the enhancement of melt strength of HDPE. These results demonstrate that xHDPE should be prepared by peroxide modification in a compression mold.

Further, it was found from linear viscoelastic measurements that the xHDPE, which enhances the melt strength to a great degree, exhibits constant  $\tan \delta$  irrespective of frequencies. Moreover, the relaxation modulus was represented by a scaling law as  $G(t) = St^{-n}$ . Furthermore, the trapped entanglements contribute to generating stress during stretching rather than the crosslink points. These mechanical properties demonstrate that the xHDPE is characterized as a critical gel at sol-gel transition.

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