

Crystallization and the Mechanical and Rheological Properties of Decrosslinked–Crosslinked-High-Density Polyethylenes Using a Supercritical Fluid

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ABSTRACT: The crystallization, and mechanical and rheological properties of decrosslinked–crosslinked-high-density polyethylenes using supercritical methanol were investigated by DSC, WAXS, DMTA, and UDS. Crosslinked high-density polyethylenes were successfully decrosslinked in a supercritical methanol condition. The residual gel content of the decrosslinked samples decreased with the reaction temperature. The crystallization behavior, mechanical, and rheological properties of the decrosslinked samples were influenced considerably by the gel content. As the gel content increased, the

network gel structure restricted the chain mobility of polymer molecules in the melt state and hindered their crystallization. Thus, the nonterminal yield behavior in the melt state was enhanced and the crystallinity decreased. The dynamic elastic modulus of the decrosslinked sample in solid state increased with the increase in the crystallinity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2090–2094, 2011

Key words: decrosslinking; supercritical methanol; polyethylene; crystallization; rheology

INTRODUCTION

Recycling of thermosetting polymers such as crosslinked polyethylene and epoxy resin has been garnered great attention owing to the deep consideration given to environmental pollution and to resource conservation efforts around the world.^{1–7} However, to date, most industrial waste containing thermosetting polymers has not been recycled because there is no method to process this waste into other useful materials due to poor fluidity and moldability.

Recently, an eco-friendly supercritical fluid process technique was introduced as a recycling method to transform crosslinked polymers into thermoplasticized polymers.^{2–9} Tagaya et al. reported that epoxy resin and polyetheretherketone resin were decrosslinked into a thermoplasticized material in subcritical and supercritical water.³ Goto and Yamazaki reported that silane-crosslinked polyethylene was depolymerized by selective decomposition of the

siloxane bond, which served as a crosslinking element in supercritical methanol or water.^{6,7} Watanabe et al. reported that the crosslink junctions of chemically crosslinked polyethylene with dicumyl peroxide were selectively decomposed using supercritical water in a process in which linear polyethylene was obtained.^{8,9} In previous articles, the authors developed a kinetics model for the decrosslinking reaction of crosslinked low-density polyethylene on the basis of experimental results in which the reaction rate was linearly proportional to the gel concentration and related exponentially to the temperature.¹⁰ The decrosslinking reaction was in good agreement with first-order reaction model with a kinetic constant of 0.867 cm³/mg min and an activation energy of 578 kJ/mol. The decrosslinked polyethylenes reacted under appropriate conditions showed mechanical and rheological properties that were comparable to those of neat low-density polyethylene.¹¹ However, the crosslinked low-density polyethylene foams contained a considerable amount of additives. The properties of the decrosslinked polymers such as crystallization and mechanical property were considerably dominated by the undesirable noise that was caused by the additives such as pigments and foaming agents.

In this work, to investigate the effect of the decrosslinking on the properties of crosslinked polyethylene such as crystallization, rheological and

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mechanical properties, decrosslinking reaction using supercritical methanol is applied to the crosslinked high-density polyethylenes that do not contain any further additives except for the crosslinking agents. The relationship between the crystallization, mechanical and rheological properties, and the degree of decrosslinking of the crosslinked polymers are investigated in detail.

EXPERIMENTAL

Materials

The crosslinked high-density polyethylene (XHDPE) pipes were supplied by Mikwang Chemical Co. in South Korea. The crosslinked polyethylene had a gel fraction of 88%. The XHDPE was manufactured via a silane-mediated crosslinking reaction of high-density polyethylene (Lutene-H XL1800). The virgin high-density polyethylene (HDPE) with a density of 0.95 g/cm³ and melt flow index of 2.0 g/10 min was purchased from LG Chemicals in South Korea. Methanol (99.5%, Samchun Chemical) was used as supercritical media, and xylene (Sigma-Aldrich) as a solvent for the extraction of the decrosslinked XHDPE.

Apparatus and supercritical methanol reaction

A batch reactor made of stainless steel (SUS316) described in previous article was designed to perform the decrosslinking of XHDPE under supercritical methanol.¹¹ Reaction was carried out as follows: a piece of XHDPE of 50 g and methanol of 100 mL were charged in the 500 mL stainless steel reactor. A piece of XHDPE with a size of 1 to 5 mm was prepared by chopping of the crosslinked polyethylene pipe. Nitrogen was purged into the reactor for degassing oxygen at room temperature. The reactor was heated to target supercritical condition to start decrosslink XHDPE and kept for 5 min at target reaction temperature and then cooled to room temperature by cold water to terminate the reaction. The pressure at target reaction temperature was way above the methanol supercritical point of 240°C and 7.93 MPa. Reaction temperature was ranged from 320 to 380°C. After the supercritical reaction, the treated XHDPE were filtered and dried in vacuum oven.

Characterizations

The gel content of the decrosslinked XHDPE was evaluated by eq. (1).

$$F_{\text{gel}} = w/w_0 * 100 \quad (1)$$

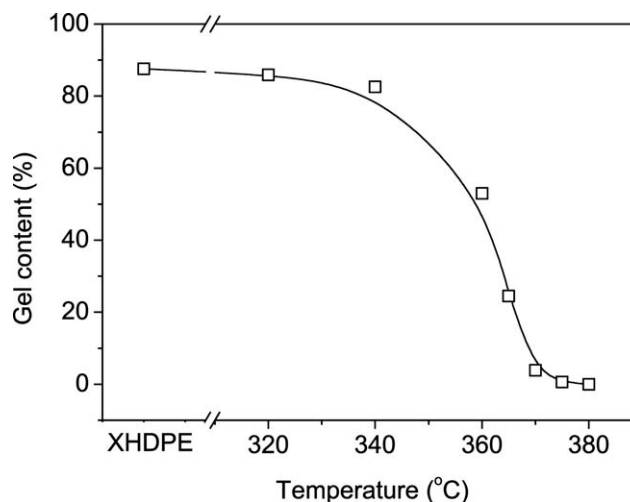


Figure 1 Gel content of the XHDPEs decrosslinked at various reaction temperatures.

Here, w_0 and w are the weight of the treated XHDPEs before and after solvent extraction, respectively. Extraction was performed using a xylene medium under the reflux condition for 12 h. DSC thermographs were measured at 10°C/min second heating using a Du Pont DSC 2950 device. To erase sample preparation history, samples were preheated to 180°C and annealed for 10 min and then cooled to 50°C at 10°C/min cooling rate before test. Synchrotron WAXS patterns were obtained at a Beamline 3C2 (Pohang Light Source, PLS) at a scanning rate of 4°/min. DMTA (dynamic mechanical thermal analyzer) tests were performed using TA Instruments DMTA Q800 device that evaluated the solid mechanical properties. For DMTA and WAXS tests, every sample was prepared by hot-press molding at 220°C after 10 min annealing. The viscoelastic properties were measured by Physica UDS 200 in oscillatory dynamic shear mode with 25 mm parallel plates at 200°C under a nitrogen atmosphere. Gap length was 1 mm. The dynamic viscoelastic tests of the XHDPEs decrosslinked below 365°C could not be measured owing to their poor fluidity. All rheological tests were performed in the linear regime.

RESULTS AND DISCUSSION

Figure 1 shows the gel content of the decrosslinked XHDPE at various reaction temperatures. The reaction temperature was varied from 320 to 380°C. The reaction time was 5 min and the error tolerance for the gel fraction was $\pm 3\%$. The initial XHDPE had a gel content of 88%. The residual gel content depended on the reaction temperature. The decrosslinking reaction scarcely proceeded until 340°C; hence, the gel content was maintained in excess of 80%. At $\sim 365^\circ\text{C}$, the gel content suddenly dropped,

and above 375°C, the gel disappeared. As a result of FTIR measurements (not shown here), it was confirmed that there existed no chemical side reaction except for the depolymerization reaction. Unfortunately, the molecular weight of the decrosslinked XHDPEs could not be measured because they had scarcely been soluble in the eluent (trichlorobenzene) for high temperature GPC test even at high temperature.

Figure 2 shows the dynamic storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) curves of neat HDPE and the decrosslinked XHDPEs in a molten state. The rheological properties of the XHDPE and the decrosslinked XHDPEs at a low temperature were not measured owing to the poor moldability. The measurements were performed at 200°C. G' , G'' , and η^* of the decrosslinked XHDPEs decreased with the reaction temperature. G' , G'' , and η^* of neat HDPE were comparable with those of the XHDPEs decrosslinked at 360°C and 365°C. The decrosslinked XHDPEs showed a faster decrease in G' , G'' , and η^* especially at a low frequency as the reaction temperature increased. This stemmed from the difference in the terminal slope of G' and G'' . Generally, in a liquid-like low-frequency region known as a terminal region, the power law linear viscoelastic slopes of a monodisperse flexible homopolymer can be expressed as $G' \propto \omega^2$ and $G'' \propto \omega$ (and $\eta^* \propto \omega$).¹² The terminal slope in G' and G'' can be affected by crosslinking,¹³ the molecular weight distribution,^{14,15} and the chain architecture.^{16,17} A smaller terminal slope indicates a stronger elastic feature. The terminal slopes of G' and G'' of the decrosslinked sample became steeper as the reaction temperature increased. The presence of elastic gel enhanced the nonterminal elastic behavior at the melt. Therefore, the increase in the terminal slope of the treated XHDPEs with the reaction temperature represents clear evidence of successful decrosslinking of the XHDPE in the supercritical methanol.

Figure 3 shows the DSC thermographs of decrosslinked XHDPEs using supercritical methanol at various temperatures. Neat HDPE and XHDPE were also compared with the decrosslinked. All curves were measured at the second heating with heating rate of 10°C/min. Every sample had one melting endothermic peak, indicating a unimodal lamella. The initial XHDPE had a melting temperature T_m of 121.6°C. The decrosslinked XHDPEs had a little higher T_m value than XHDPE. As the reaction temperature increased, T_m of decrosslinked XHDPEs approached toward that of virgin HDPE about 135°C. The crystallinity $X_{c,DSC}$ was calculated from heat of fusion ΔH_m according to the following eq. (2):

$$X_{c,DSC} = \Delta H_m / \Delta H_{m,PE} \quad (2)$$

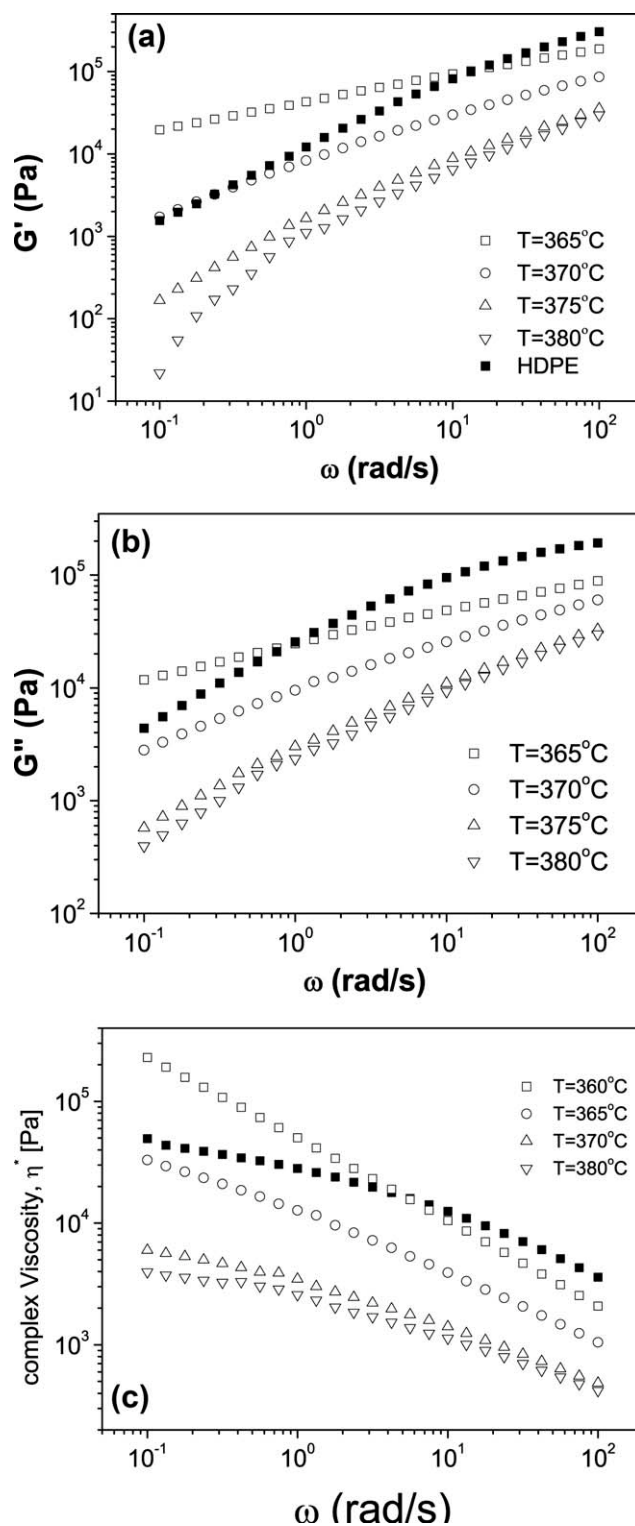


Figure 2 (a) Storage modulus (G'), (b) loss modulus (G''), and (c) complex viscosity (η^*) of neat HDPE and XHDPEs decrosslinked at various reaction temperatures.

Here, $\Delta H_{m,PE} = 277$ J/g was the theoretical heat of fusion of perfect crystalline high-density polyethylene.¹⁸ The $X_{c,DSC}$ value of the decrosslinked XHDPEs from the DSC results will be discussed in a later section.

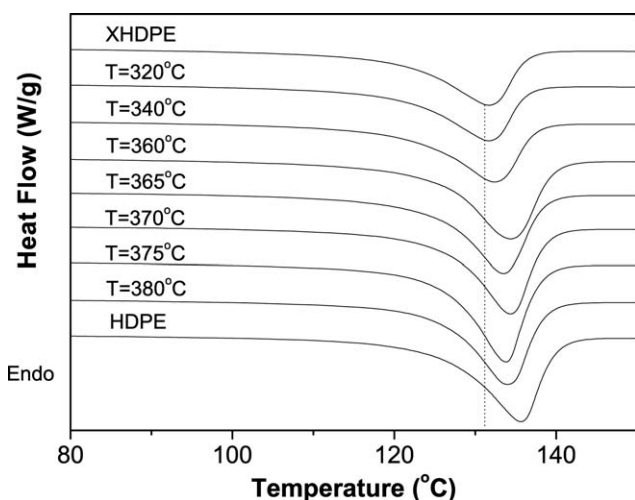


Figure 3 DSC thermographs of HDPE and XHDPEs decrosslinked at various reaction temperatures.

Figure 4 shows synchrotron WAXS patterns of XHDPE and decrosslinked XHDPE at 380°C. Both samples had three characteristic scattering peaks: the (110) and (200) plane reflection peaks from the orthorhombic unit cell of the polyethylene and a broad amorphous halo from the amorphous portion.¹⁹ The decrosslinked XHDPE at 380°C had a larger (110) reflection peak but a smaller amorphous halo than the XHDPE. For a quantitative comparison, the crystallinity $X_{c,WAXS}$ was calculated from WAXS data using the following eq. (3):

$$X_{c,WAXS} = (I(110) + I(200))/I_{total} \quad (3)$$

In this equation, $I(110)$ and $I(200)$ are the intensity of the (110) and (200) reflections, respectively, and I_{total} is the total observed intensity.

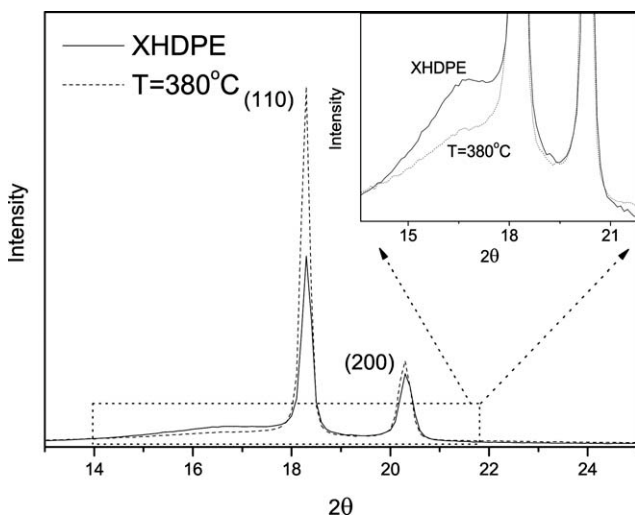


Figure 4 Synchrotron WAXS curves of XHDPEs before and after decrosslinking at 380°C.

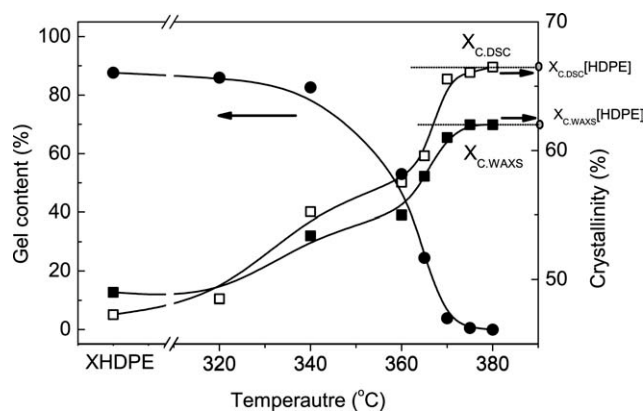


Figure 5 Gel content (●) and crystallinity of the XHDPEs decrosslinked at various reaction temperatures. $X_{c,DSC}$ (□) and $X_{c,WAXS}$ (■) represent the crystallinities evaluated from the data of WAXS and DSC, respectively.

Figure 5 shows the gel fraction, $X_{c,DSC}$ and $X_{c,WAXS}$ values of decrosslinked XHDPEs at various temperatures. $X_{c,WAXS}$ from the WAXS results was fairly consistent with $X_{c,DSC}$ from the DSC results. The $X_{c,DSC}$ and $X_{c,WAXS}$ of the initial XHDPE were 49% and 46%, respectively. The crystallinity of the decrosslinked XHDPEs slowly increased with the reaction temperature until 340°C. At ~ 365°C, the crystallinity increased in steps and above 375°C, the crystallinity was nearly saturated. The saturated crystallinity is equivalent to the crystallinity of virgin HDPE. The abrupt increase zone in crystallinity corresponded to the abrupt decrease zone in gel content. This indicates that the network structure in the gel lessens the crystallinity of the XHDPEs. It must be from the fact that the network gel structure restricts the chain mobility of polymer molecules in melt state and hinders their crystallization.^{20,21} Hence, the crystals formed in a restricted condition,

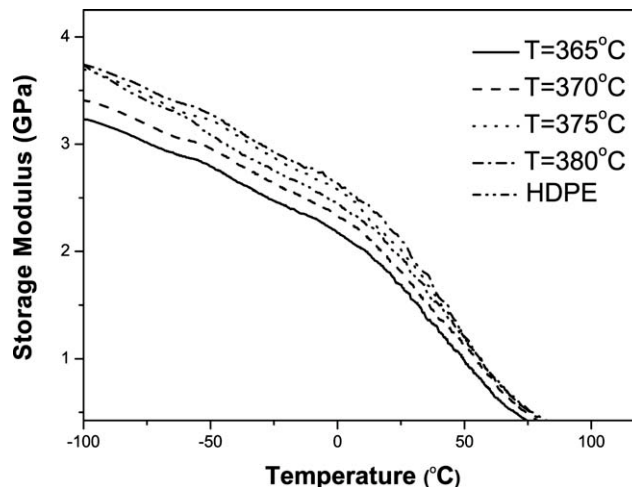


Figure 6 DMTA curves of HDPE and XHDPEs decrosslinked at various reaction temperatures.

as in a XHDPE samples with a high-gel content, had a lower T_m value compared with those crystallized in a gel-free decrosslinked XHDPE or virgin HDPE.

Figure 6 shows dynamic storage modulus (E') of decrosslinked XHDPEs and virgin HDPE at various temperatures. E' of the XHDPE and decrosslinked XHDPEs at a low temperature were not measured due to their poor moldability. The storage modulus of the XHDPEs gradually decreased with the temperature. A steep drop was noted at the glass transition temperature T_g . However, glass transition temperature of the decrosslinked samples did not be affected by the reaction temperature. In contrast, the storage modulus monotonously increased with the decrosslinking reaction temperature. Virgin HDPE had the almost same dynamic storage modulus as the sample decrosslinked at 375°C. It must be caused by the increase in the crystallinity. The decrosslinked XHDPEs studied here were a semicrystalline polymer in which the crystallinity closely depended on the crosslinking density.^{20,21} In general, crystalline region has much higher stiffness than rubbery regions. Therefore, the XHDPE decrosslinked at a high temperature had a higher storage modulus, E' , compared with the sample decrosslinked at a lower temperature because the former had higher crystallinity than the latter.

CONCLUSIONS

Crosslinked high-density polyethylenes were successfully decrosslinked in a supercritical methanol condition. The decrosslinking reaction proceeded slowly until 340°C. At $\sim 365^\circ\text{C}$, the decrosslinking was suddenly enhanced, completing at a temperature in excess of 375°C. The crystallization, mechanical and rheological properties of the decrosslinked samples were greatly influenced by the gel content. As the gel content increased, chain mobility of polymer molecules was disturbed by the network structure. Hence, the nonterminal yield behavior was enhanced and the crystallinity decreased. The dynamic elastic modulus increased with an increase in the crystallinity.

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