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Physical and Rheological Properties of Thermoplasticized Crosslinked-Polyethylene Foam in Supercritical Methanol

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Abstract: The physical and rheological properties of thermoplasticized irradiation-crosslinked polyethylene foam using supercritical methanol treatment were investigated by GPC, FTIR, DSC, WAXS, DMTA and UDS. The polyethylene foam was selectively decrosslinked into thermoplasticized polyethylene in an appropriate supercritical methanol condition without any undesirable side reactions such as oxidation and disproportionation. The thermoplasticization was promoted with increasing reaction temperature to reach completion above 380 °C. The supercritical reaction condition affected the crystallization behavior, and mechanical and rheological properties of the decrosslinked polyethylene foam, but not its crystallographic structure or crystallinity.

Keywords: decrosslinking, thermoplasticization, crosslinked polyethylene foam, supercritical methanol, rheology.

Introduction

Thermoplasticization of thermosetting polymers such as crosslinked polyethylene and epoxy resin for recycling has been taken a great attention because of deep consideration of prevention of environmental pollution and of resource conservation over the world.[1-8] However, even this moment, most industrial wastes of crosslinked polymers have been burned as fuel or disposed of in landfills because there is no method to process them into other useful material due to their low thermoplasticity and poor moldability.

Recently, a handful of scientists have tried to develop a recycling method to transform crosslinked polymers into thermoplasticized ones by using supercritical fluid.[2-9] Tagaya *et al.* reported that epoxy resin and polyetheretherketone resin were depolymerized in sub and supercritical water.[3] Genta *et al.* reported depolymerization of poly(ethylene terephthalate) in supercritical methanol.[4] Goto and Yamazaki reported that silane-crosslinked polyethylene was depolymerized by selective decomposition of siloxane bond playing as a crosslinking element in the supercritical methanol or water.[6,7] Watanabe *et al.* reported that crosslink junctions of chemically crosslinked polyethylene with dicumyl peroxide were selectively decomposed by using supercritical water and linear polyethylene was obtained.[8,9]

In our previous article, for the first time, we proposed a kinetics model for the decrosslinking reaction of crosslinked polyethylene on the basis of the experimental results that reaction rate was linearly proportional to the gel concentration and related exponentially with temperature.[10] The decrosslinking reaction agreed well with first order reaction model with kinetic constant of 0.867 $cm^3/mg \cdot min$ and activation energy of 578 kJ/mol. However, researches on decrosslinking of thermosetting polymers with supercritical fluids are still in its primary stage. Physical and rheological properties of decrosslinked polymers have been not known well yet.

In this article, a sufficient amount of supercritically decrosslinked polyethylene foam was obtained by using scale-up version 500 mL reactor of previous experiment for the physical and rheological tests. Physical and rheological properties of the decrosslinked polyethylene foams using supercritical methanol have been investigated in detail.

Experimental

Materials. Low density polyethylene (LDPE), and irradiation-crosslinked low density polyethylene foam (XLPE) were supplied from Youngbo Chemical in South Korea. The commercial XLPE foam was manufactured via irradiation-

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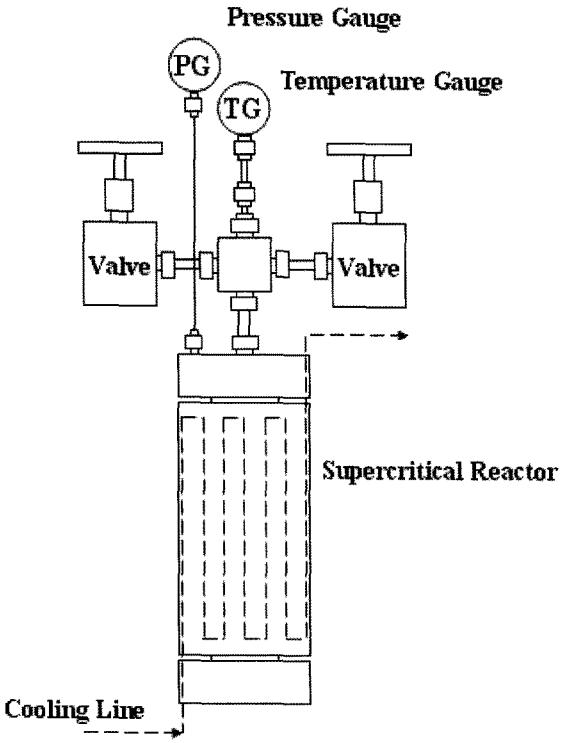

Figure 1. Schematic of a batch reactor for supercritical methanol treatment.

induced crosslinking of the compounded LDPE which is including a sufficient foaming agent and a quite amount of titanium dioxide, zinc oxide and dicumylperoxide. The irradiation was exposed using a β-ray generated by the dynamitron accelerator [Nisshin high voltage (NHV)] with the acceleration voltage of 1 MeV. Irradiation-crosslinked polyethylene had 65% gel fraction. A chunk of XLPE foam with 0.6 to 1 mm size used in decrosslinking reaction was made via roll milling treatment at 100 °C in order to lessen the volume of XLPE foam and following chopping. Methanol (99.5%, Samchun Chemical) was used as supercritical media and xylene (Sigma-Aldrich) as a solvent for extraction of de-crosslinked XLPE in order to measure gel-fraction.

Apparatus and Supercritical Methanol Reaction. Figure 1 shows a schematic of a batch reactor designed for supercritical methanol treatment of XLPE. The stainless steel (SUS316) reactor had 500 mL interior vessel volume and thermocouple and pressure gage attached to the reactor, which was scale-up version of previous experiment in order to make a sufficient amount of samples for the physical and rheological tests.[10] Temperature was controlled by heating furnace wrapping around the reactor vessel. Reaction procedure was as follows: a chunk of XLPE 50 g and methanol 100 g were charged in the reactor. Nitrogen was purged into the reactor for degassing oxygen at room temperature. The reactor was heated to target supercritical condition to start decrosslink XLPE and kept for 10 min at target reaction temperature and then cooled to room temperature by cold water to terminate the reaction. The treated XLPEs were filtered and dried at vacuum oven.

Characterizations. Gel fraction, F_{gel} of the treated XLPE was evaluated by eq. (1).

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

where w_0 and w are the weight of XLPEs before and after solvent extraction, respectively. Extraction was performed using xylene medium at 110 °C for 12 h. Molecular weight and molecular weight distribution of the extracted were measured by high temperature GPC (Waters, Model 150C: Column Mixed B) with polystyrene standard and TCB+ 0.01% BHT solvent. FTIR was measured by Perkin Elmer Spectrum GX. DSC thermographs were measured at 10 °C/min heating and cooling rates by Du Pont DSC 2950. WAXS patterns were obtained by a RINT 2000 wide angle goniometer (Rigaku, Japan) using Cu Kα radiation (λ=0.15406 nm) with a scanning rate of 4°/min. DMTA (dynamic mechanical thermal analyzer) tests were performed by using TA Instrument DMTA Q800 to evaluate solid mechanical property. Rheological measurements were performed by Physica UDS 200 in the oscillatory mode with 25 mm parallel plates from 140 to 220 °C under nitrogen atmosphere. All data were obtained in the linear regime.

Results and Discussion

Gel content and molecular weight of the treated XLPEs at various temperatures were presented in Figure 2 and Table I. Reaction temperature was ranging from 350 to 400 °C where the pressure was around 20 to 23 MPa. The reaction condition was way above critical point of methanol of 240 °C and 7.93 MPa. Initial XLPE had 65% gel fraction. Gel fraction of the decrosslinked XLPE monotonously reduced with

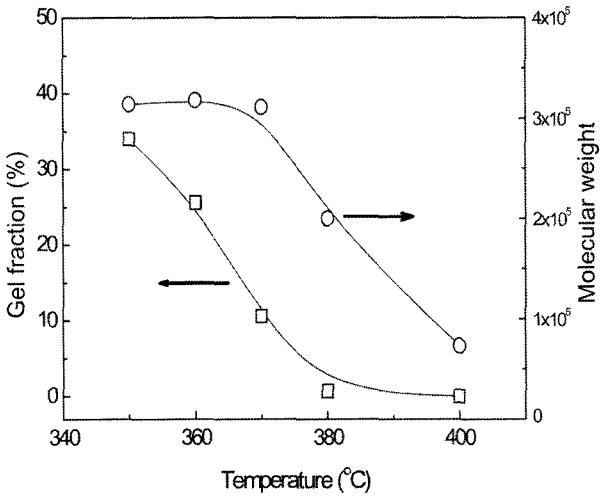

Figure 2. Gel content and molecular weight of the decrosslinked XLPEs at various reaction temperatures.

Table I. Characterizations of LDPE and XLPEs before and after Supercritical Methanol Treatment at Various Temperatures

Temperature (°C)	Gel Content (%)	GPC		DSC			WAXS		
		M_w	PDI	T_c (°C)	T_m (°C)	$X_{c,DSC}$	a (Å)	b (Å)	$X_{c,WAXS}$
XLPE	60	-	-	88.5	98.9	0.32	7.49	4.98	0.52
350	34.0	314,000	12.6	91.2	103.0	0.49	7.58	5.03	0.54
360	25.6	318,000	11.1	90.1	102.1	0.50	7.55	4.97	0.51
370	10.6	311,000	12.1	91.1	102.6	0.50	7.61	5.06	0.53
380	0.7	200,000	13.0	92.1	103.0	0.55	7.59	5.04	0.54
400	0	73,000	6.9	93.9	103.3	0.40	7.57	5.02	0.55
LDPE	0	349,000	7.0	87.2	100.7	0.48	7.55	5.01	0.55

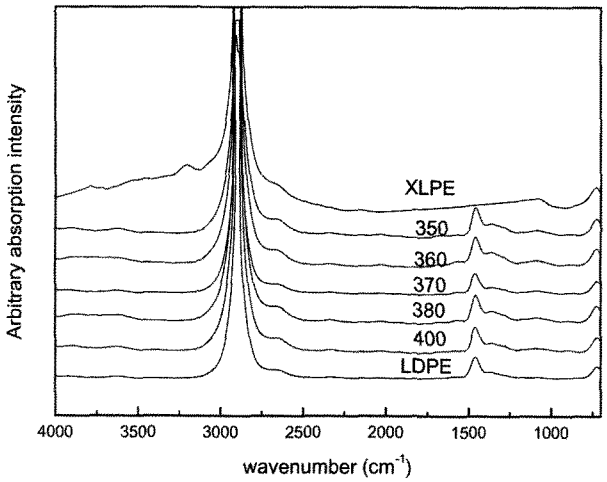

Figure 3. FTIR spectra of LDPE and the decrosslinked XLPEs at various temperatures.

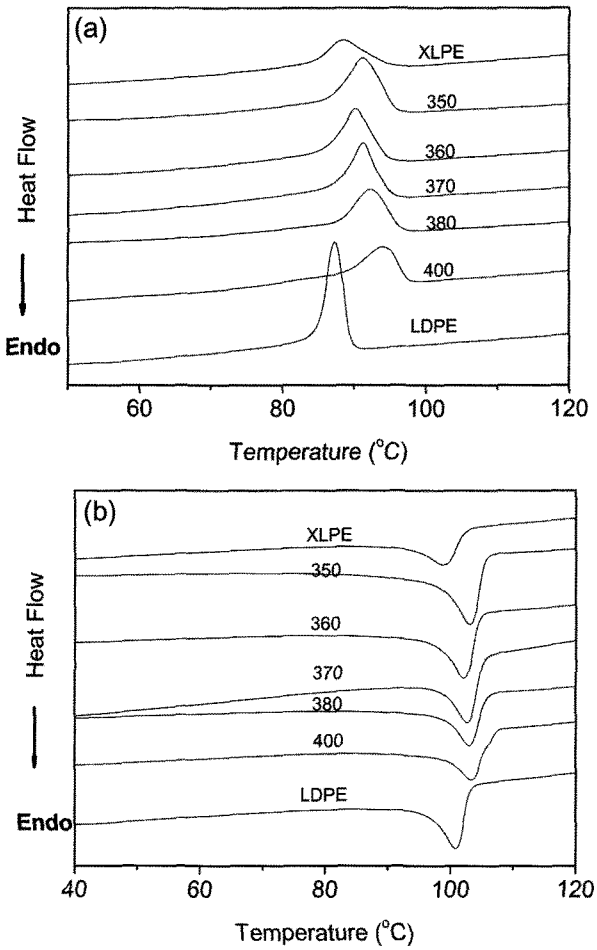

Figure 4. DSC thermographs of LDPE and the decrosslinked XLPEs (a) at cooling scan and (b) heating scan.

reaction temperature and reached to zero around 380 °C. In contrast, molecular weight of the extracted was kept equal to that of LDPE up to 370 °C and then diminished with the temperature.

Figure 3 shows FTIR spectra of LDPE and XLPEs before and after supercritical treatment at various temperatures. The decrosslinked was denoted by reaction temperature in the figure. The decrosslinked XLPEs had the same FTIR pattern as LDPE. Each sample just has two characteristic peaks of polyethylene: 2800-3000 cm^{-1} peak of sp^3 C-H stretching and 1450 cm^{-1} peak of CH_2 bending. It was not observed that new reflection peaks such as C=C (1600-1650 cm^{-1}) or C=O (1600-1800 cm^{-1}) indicating undesirable side reaction such as oxidation and disproportionation.

From these results, it could be concluded that decrosslinking reaction of XLPE was promoted with reaction temperature and completed above 380 °C without any side reaction in the supercritical methanol. In addition, XLPE was apt to be fairly selectively decomposed at the crosslink points, not at random sites in the supercritical condition. Therefore, the decrosslinked was kept on the level of molecular weight of LDPE up to 370 °C. One possible reason for the selective decomposition could be explained in the terms of the formation of carbon radicals. Because tertiary radicals produced from qauternary carbons at crosslink point have longer lifetime than secondary or primary radicals from other carbons, the crosslink points must be more vulnerable sites in the thermal decomposition than other carbons, creating a selec-

tive decomposition.[10]

Figure 4 shows crystallization curves and melting curves of LDPE and XLPEs before and after supercritical treatment. All curves were measured in the second run with the heating and cooling rates of 10 °C/min. All DSC data were listed in Table I. In Figure 4(a), the treated XLPEs had higher crystallization temperature than XLPE. Partially or fully decrosslinked XLPE may have higher degree of freedom in chain mobility than XLPE because of lower gel fraction. It appeared to help the treated XLPE start to crystallize higher temperature. Hence, crystallization temperature of the crosslinked increased with the reaction temperature. In addition, the decrosslinked had higher crystallization temperature than LDPE as well. It could be understood by the fact that the commercial XLPE was including a variety of additives such as pigments and foaming agents, and the additives could play as an effective nucleation agent. In Figure 4(b), every sample had one melting endothermic peak, indicating a unimodal lamella. LDPE had melting temperature of 100.7 °C. The decrosslinked had higher T_m than LDPE and XLPE as well. Crystallinity $X_{c.DSC}$ was calculated from heat of fusion, ΔH_m, using the following eq. (2):

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

where $\Delta H_{m.PE}$=277 J/g was the theoretical heat of fusion of perfect crystalline high density polyethylene.[11] The decrosslinked had the almost same crystallinity about $X_{c.DSC}$=0.5 as LDPE.

Figure 5 shows WAXS patterns of LDPE and XLPEs before and after supercritical treatment. Each sample had characteristic three scattering peaks: (110) and (200) plane reflection peaks from orthorhombic unit cell of polyethylene and a broad amorphous halo from amorphous portion. Crystallinity $X_{c.WAXS}$ was calculated from WAXS using the following eq. (3):

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

where $I(110)$, $I(200)$ were intensity of (110) and (200) reflections and I_{total} was the total observed intensity. The unit cell dimensions were calculated using Bragg's law in eq. (4) and orthorhombic plane distance relationship in eq. (5).

$$d_{hkl} = \frac{\lambda}{2\sin\theta_{hkl}} \quad (4)$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (5)$$

All WAXS results were also summarized in Table I. LDPE had orthorhombic lattice dimensions of a=7.39 Å, b=4.97 Å and crystallinity $X_{c.WAXS}$ = 0.55. The decrosslinked XLPEs had the almost same unit cell dimensions and $X_{c.WAXS}$ as the LDPE. In addition, the crystallinity from WAXS, $X_{c.WAXS}$ was pretty consistent with that from DSC, $X_{c.DSC}$.

Figure 6 shows storage moduli (E') of LDPE and the decrosslinked XLPEs at various temperatures. Storage modulus of XLPE was not measured because of its poor moldability. Storage modulus of the decrosslinked gradually decreased with the temperature until a steep drop appeared at the glass transition. For the comparison, storage moduli of the decrosslinked at -80 °C were presented in Figure 7. LDPE (solid line) was compared with the decrosslinked. Storage modulus of the decrosslinked slowly decreased with reaction temperature. The decrosslinked had a little higher storage modulus than LDPE up to 360 °C, but lower storage modulus than LDPE above 370 °C. Nonetheless, the decrosslinked XLPE had comparable storage modulus with LDPE up to 380 °C. It could be understood in terms of gel fraction and molecular weight of the decrosslinked. The decrosslinked XLPE studied in the work was a semicrystalline polymer which had about 50% crystalline portion and 50% amorphous portion in spite of different crosslinking

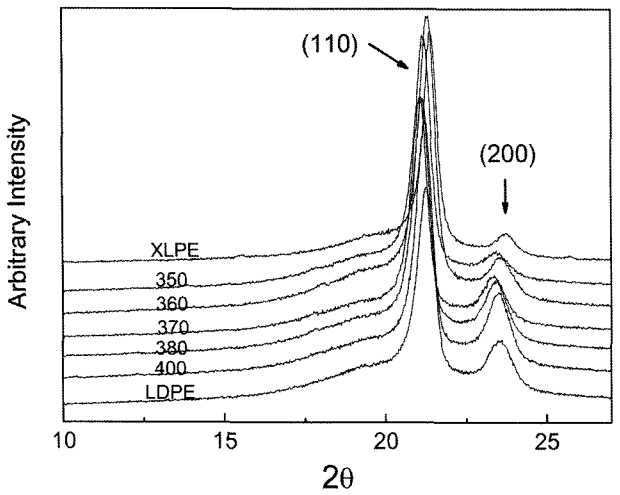

Figure 5. WAXS patterns of LDPE and the decrosslinked XLPEs at various temperatures.

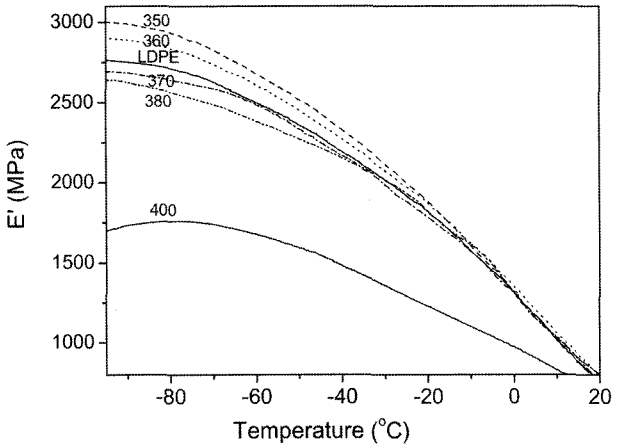

Figure 6. Storage moduli (E') of LDPE and the decrosslinked XLPEs.

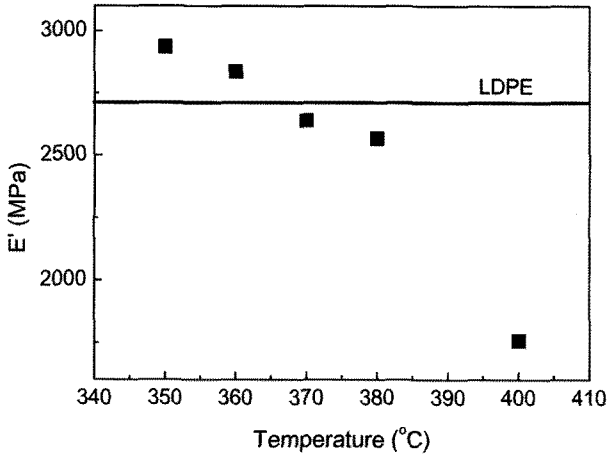

Figure 7. Storage modulus (E') of LDPE and the decrosslinked XLPEs at -80 °C.

density. The amorphous polyethylene is well known to have very low beta or gamma glass transition less than -100 °C.[11] In the temperature -80 °C, it is thought that considerable part of our sample is still in rubbery state where the modulus is able to be influenced by molecular weight and crosslinking density. Therefore, we believe that higher temperature treated sample had lower storage modulus because of lower molecular weight and lower crosslinking density. In addition, storage modulus of the decrosslinked was rarely sacrificed up to 380 °C in the supercritical reaction, because molecular weight fairly was kept on the level of molecular weight of LDPE thanks to high decomposition selectivity.

Figure 8 shows the dynamic storage moduli (G') and loss moduli (G'') master curves for LDPE and the decrosslinked XLPEs at melt state. The curves were generated by the principle of time temperature superposition. Reference temperature was 180 °C. Measurements were performed over the temperature range of 140 to 220 °C. At high frequency, LDPE had higher G' and G'' than the decrosslinked. G' and G'' of the decrosslinked slowly decreased with reaction temperature. In contrast, at low frequency, LDPE had lower G' and G'' than the decrosslinked below 360 °C. The decrosslinked showed more fast decrease in storage and loss modulus at low frequency than at high frequency as reaction temperature increased. It stemmed from the difference in terminal slope of G' and G'' listed in Table II. Terminal slope in G' and G'' could be affected by crosslinking,[12] molecular weight distribution[13,14] and chain architecture.[15,16] In general, the smaller terminal slope indicates the stronger elastic fea-

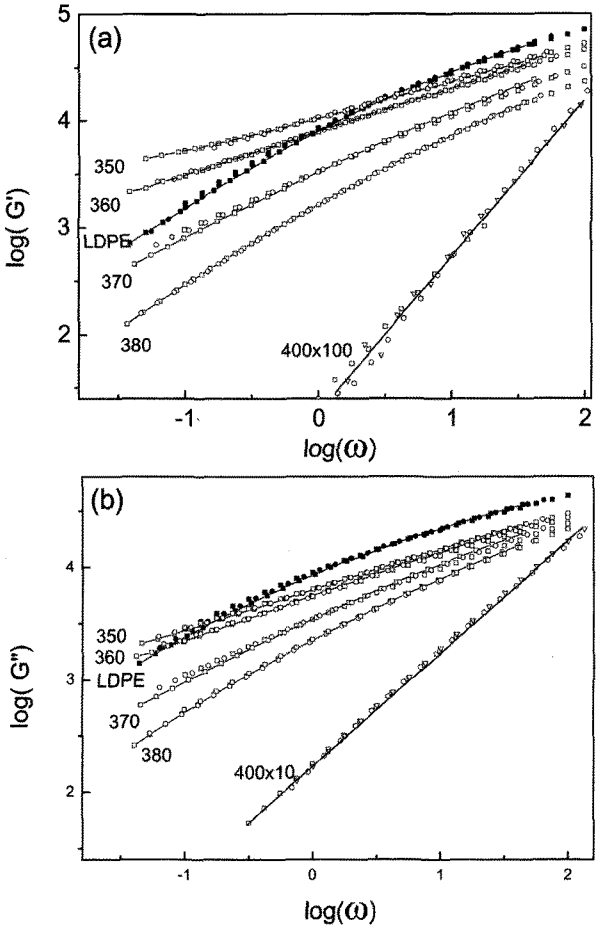

Figure 8. The master curves of (a) storage moduli (G') and (b) loss moduli (G'') of LDPE and the decrosslinked XLPEs.

ture. A monodisperse flexible homopolymer has two and one slope of G' and G'' at the terminal region, respectively.[17] LDPE had 0.77 and 0.56, which might be attributed to their high molecular weight and wide molecular weight distribution. Especially, higher molecular weight of LDPE more than 300,000 g/mol induced tremendous entanglement, producing strong elastic feature at melt state. Terminal slopes of G' and G'' of the decrosslinked became steeper as the reaction temperature increased. The presence of elastic gel helps to enhance non-terminal elastic behavior at the melt.[12] Therefore, the increase in terminal slope of the treated XLPE with the reaction temperature must be a clear evidence of the decrosslinking in the supercritical methanol.

Table II. Terminal Slopes of G' and G'' versus ω for LDPE and the Decrosslinked XLPEs

Terminal Slope	LDPE	350	360	370	380	400
G'	0.77	0.34	0.4	0.54	0.77	1.45
G''	0.56	0.35	0.37	0.48	0.65	1.0

Conclusions

The irradiation-crosslinked polyethylene foam was successfully decrosslinked into the thermoplasticized polyethylene without any undesirable side reaction using supercritical methanol. The thermoplasticization was enhanced with reaction temperature and completed above 380 °C. It was possible to obtain the completely thermoplasticized polyethylene having comparable crystallographic, mechanical and rheological properties with raw LDPE at appropriate supercritical methanol condition.

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