

## Continuous Supercritical Decrosslinking Extrusion Process for Recycling of Crosslinked Polyethylene Waste

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**ABSTRACT:** This work demonstrates that extrusion process can be used as a continuous reactor for the recycling of crosslinked polyethylene (XLPE) via supercritical methanol decrosslinking reaction. The multistage single screw extruder ( $L/D = 36$ ,  $D = 40$  mm) with methanol injection pump was customized for the continuous supercritical decrosslinking reaction. Reaction temperature was ranged from 360°C to 390°C. The amount of methanol was varied from 0 to 7 mL/min. The extruder provided the crosslinked polymers with the supercritical conditions of methanol during continuous process. The gel content of XLPE decreased with the increase in the reaction temperature and methanol content. Although XLPE experienced supercritical methanol for less than 2 min retention time in the continuous supercritical extruder, it was completely decrosslinked above 390°C at the methanol feeding rate of 7 mL/min. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41442.

**KEYWORDS:** crosslinking; degradation; polyolefins; thermosets; viscosity and viscoelasticity

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### INTRODUCTION

Plastics have been massively used in various industrial fields because of their many advantages, such as light weight, low cost, good mechanical features, and excellent insulation properties against heat and electricity.<sup>1,2</sup> Because of the large-scale consumption of plastics, recycling of waste plastics has taken a growing attention in the view of environmental pollution reduction and conservation of resources. Recycling technologies for most thermoplastic polymers have been well established.<sup>3–7</sup> In contrast, the recycling of thermosetting polymers still remains a great challenge. Most of thermosetting polymers, including epoxy, unsaturated polyester, and crosslinked polyethylene (XLPE), have been incinerated or land filled because of difficulty in their processing and low fluidity resulting from their insoluble and infusible characteristics that prohibit recycling.<sup>8–10</sup>

Recently, several research groups reported that supercritical fluids can be used as a reaction medium for the depolymerization

reaction of several condensation polymers and decrosslinking reaction of XLPE.<sup>11–25</sup> Polyethylene terephthalate has been depolymerized via hydrolysis or solvolysis reactions in supercritical water and methanol medium.<sup>8</sup> Polycarbonate was depolymerized into dimethyl carbonate and bisphenol A in supercritical methanol and NaOH.<sup>18</sup> Watanabe et al. demonstrated that XLPE can be completely decrosslinked and converted into thermoplastic PE using supercritical water.<sup>11</sup> Goto et al. reported that silane-XLPE could be depolymerized through selective decomposition of the siloxane bonds in supercritical methanol or water.<sup>12</sup> In our previous studies, we also observed that the irradiation-crosslinked, the silane-crosslinked, and the peroxide-crosslinked PE could successively be decrosslinked into the thermoplastic PE using supercritical methanol.<sup>19–25</sup> The decrosslinking reaction rate was observed as linearly proportional to the gel content and exponentially related to the reaction temperature. The supercritical decrosslinking corresponded to the first-order reaction with kinetic

constant of  $0.867 \text{ cm}^3/\text{mg min}$  and activation energy of  $578 \text{ kJ/mol}$ . The decrosslinked PE products provided molecular weight, and mechanical and rheological properties comparable with those of neat PE.<sup>23</sup> Kwon et al. revealed that the recycled PE could be reused like a virgin PE in the foam production process. The foams of decrosslinked PE produced in this way had a viable cellular structure and physical properties comparable with those of conventional neat LDPE foams.<sup>20</sup>

In most of the previous studies, however, the depolymerization and decrosslinking reactions using supercritical fluids were performed in the batch reactors. The batch process is time-consuming and cost-inefficient. To establish the recycling process at industrial scale, continuous supercritical reaction process needs to be developed. Recently, Goto et al. reported the recycling of silane-crosslinked PE through using the extruder at  $335^\circ\text{C}$ .<sup>13</sup> However, it just provided the limited information on the continuous extruder reactor and reaction conditions. The detailed information about continuous recycling of crosslinked polymers with extruder is still unclear.

In this work, we demonstrated that an extruder can be used as a reactor for the supercritical methanol decrosslinking reaction of peroxide-crosslinked PE, XLPE. The C–C crosslinking bond of peroxide-crosslinked PE has much better thermal stability than the silane-crosslinking bond in silane-crosslinked PE.<sup>12–14,19–24</sup> The multi-stage single screw extruder specially designed for peroxide crosslinked PE provides XLPE with the reliable supercritical conditions of methanol during continuous extrusion. The XLPE samples were successfully decrosslinked in the continuous supercritical extruder.

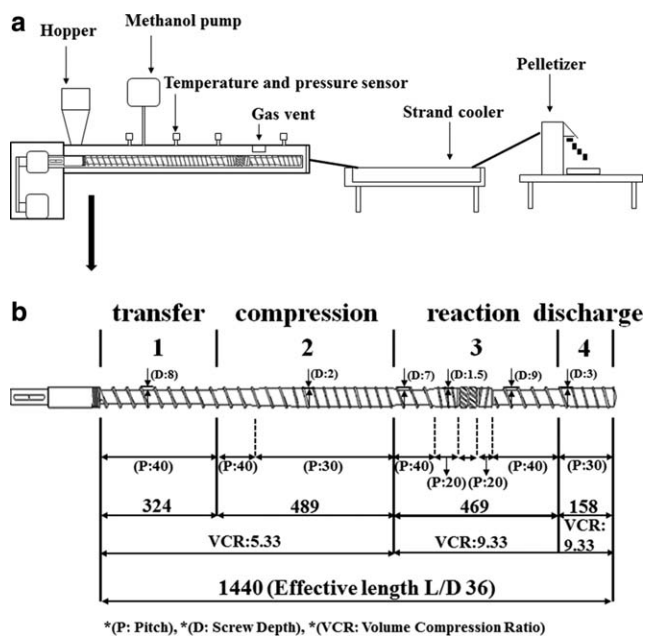
## EXPERIMENTAL

### Materials

Chemically crosslinked LDPE cable coating with 82.3% of gel contents was supplied from LS Cable & System, Korea. The XLPE sample was manufactured from low density polyethylene (LDPE BC500,  $M_w = 221,000 \text{ g/mol}$ ,  $\text{PDI} = 7.42$ ,  $\text{MI} = 0.3 \text{ g/min}$ , density =  $0.921 \text{ g/cm}^3$ , LG Chemical, Korea) via the peroxide crosslinking method using dicumyl peroxide.<sup>26–28</sup> The waste XLPE samples were pellets in approximately 5 mm particle size. Methanol (99.5%, Daejung Chemical, Korea) was used as supercritical reaction medium and xylene (ACS reagent, Sigma-Aldrich, USA) as an extraction solvent for the measurement of gel contents.

### Extruder Setup and Continuous Supercritical Decrosslinking Reaction

A schematic of the continuous supercritical process system, consisting of a multistage single screw extruder, is shown in Figure 1. The extruder ( $L/D = 36$ ,  $D = 40 \text{ mm}$ , where  $L$  and  $D$  are length and diameter of screw), including a methanol injection pump, was customized by Hankook EM, Korea. A cooling bath and a pelletizer were attached to the extruder. A multistage single screw, composed of four divided zones of transfer, compression, reaction, and discharge zones, was used in the extruder barrel, as shown in Figure 1(b). The first transfer zone was in charge of feeding and transferring the XLPE waste material. The second compression zone was compressing the resin to



**Figure 1.** (a) Schematic illustration of continuous supercritical methanol process using multistage single extruder, and (b) design of multistage screw.

attain supercritical pressure conditions of methanol; therefore, screw diameter was gradually getting bigger in the second zone. Methanol was injected to the end of compression zone of the extruder with a liquid injection pump. The third reaction zone was responsible for the decrosslinking reaction of XLPE in supercritical methanol conditions. The discharge zone was for discharging the decrosslinked XLPEs. The extrudate was a form of strand so as to be pelletized and collected as samples.

The multistage single screw was divided into four different zones and compression ratios, depth of screw, and screw pitch to optimize the decrosslinking extrusion process [Figure 1(b)]. Total screw length was 1440 mm and that of transfer, compression, reaction, and discharge zones were 324, 489, 469, and 158 mm, respectively. The screw depth was designed differently between zones; which were 8 mm in the transfer zone and 2 mm in the compression zone. To increase the compression ratio and prevent the vent-up of the supercritical methanol gas, screw depth in the first zone was made deeper than that of the second zone. The volume compression ratio was also different between zones, which was 5.33 in both the first and second zones. The sample materials were introduced into the reaction zone under the increased internal pressure conditions. In the reaction zone, compression and reaction simultaneously occurred and compression ratio (9.33) increased more than that in the first and second zones by reverse screw element and change in screw pitch. Therefore, the supercritical conditions of methanol ( $T_c = 243^\circ\text{C}$ ,  $P_c = 7.93 \text{ MPa}$ )<sup>23</sup> could be attained. A reverse screw element was used at the reaction zone to elevate the internal pressure and prolong retention time of material. The reacted XLPE was passing through the discharge zone.

Methanol was vented through the gas vent in the discharge zone. The discharged product was cooled in the cooling bath

and then pelletized and collected using pelletizer. The XLPE pellets of approximately 5 mm were fed from the hopper of the extruder and screw speed was set at 60 rpm. The amount of methanol feeding was varied from 0 to 7 mL/min. When MeOH was injected over 7 mL/min, severe vent-up of resin occurred through the gas vent and feeder. The reaction temperature was set from 360°C to 390°C. Table I lists the internal temperatures and pressures of various zones monitored with thermometer and manometer. For all experimental conditions, the reaction zone satisfied the supercritical conditions of methanol. That is, all samples experienced the supercritical methanol conditions before discharging from the supercritical single screw extruder. The decrosslinked XLPE samples were denoted as the reaction temperature and the content of injected methanol. For example, when the reaction temperature ( $T$ ) and injected methanol content ( $M$ ) were 390°C and 7 mL/min, respectively, the sample was denoted as T390 M7.

### Characterizations

To quantify the degree of crosslinking, the gel contents of decrosslinked XLPEs were examined according to ASTM standard D 2765. An amount of 300 mg of pulverized sample was extracted using boiling xylene at 110°C for 12 h and then dried in vacuum oven to completely remove xylene. The gel contents of the samples were calculated as follows:

$$\text{Gel contents(\%)} = w/w_0 \times 100 \quad (1)$$

where  $w_0$  and  $w$  are the weights of the sample before and after solvent extraction, respectively. The molecular weight was measured through high temperature gel permeation chromatography (GPC 150C, Waters, USA). The sample was dissolved in trichlorobenzene at 160°C for 4 h and the extract was then passed through GPC MIXED-B column. Differential scanning calorimeter (DSC, Q200, TA Instrument, USA) was used to determine the melting temperature ( $T_m$ ). The crystalline structure and crystallinity were examined using an X-ray diffractometer (XRD, D-MAX2500-PC, Rigaku, Japan). The chemical structures of the samples were analyzed with a Fourier-transform infrared spectrophotometer (FT-IR, Spectrum GX, Perkin Elmer, USA). The rheological properties were examined with a Paar Physica Universal Dynamic Spectrometer rheometer (Anton Paar, Switzerland) in nitrogen atmosphere. In rheological measurements, a parallel-plate geometry with a diameter of 25 mm and a gap of 1.0 mm was adopted. All rheological measurements were performed in the linear viscoelastic region.

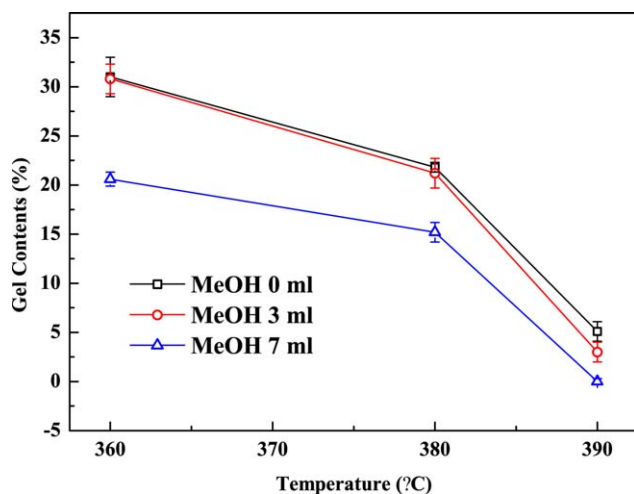
## RESULTS AND DISCUSSION

### Gel Contents of Decrosslinked XLPE

Figure 2 shows the gel contents of the decrosslinked products as a function of reaction temperature and methanol content. Pristine XLPE had a gel content of 82.3%. The amount of injected methanol was varied from 0 to 7 mL/min. Reaction temperature was set from 360°C to 390°C to prevent oxidation of PE above 390°C. It was observed that, at the constant methanol level, the gel fraction decreased with the increase in reaction temperature. At a constant temperature, the gel fraction decreased with the increase in methanol content. Gel fractions of T360M0, T380M0, and T390M0 products, which were processed at

Table I. Supercritical Decrosslinked Reaction Conditions of Each Sample

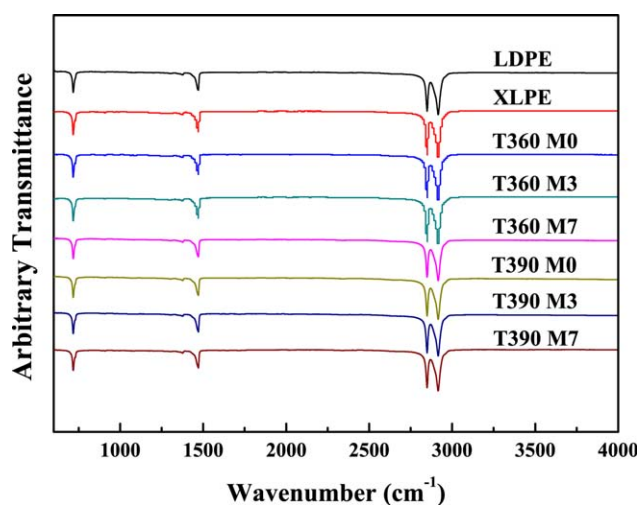
Sample	Set temp. (°C)	MeOH content (ml)	RPM of screw	Zone 1 transfer		Zone 2 compression		Zone 3 reaction		Zone 4 discharge		
				Real Temp. (°C)	Pressure (bar)	Real Temp. (°C)	Pressure (bar)	Real Temp. (°C)	Pressure (bar)	Real Temp. (°C)	Pressure (bar)	Discharge rate (g/min)
T360 M0	360	0	60	355 ± 3	5 ± 1	365 ± 3	152 ± 2	360 ± 3	95 ± 2	355 ± 3	33 ± 1	295 ± 5
T360 M3	360	3	60	355 ± 3	5 ± 1	365 ± 3	150 ± 2	360 ± 3	95 ± 2	355 ± 3	33 ± 1	297 ± 5
T360 M7	360	7	60	355 ± 3	5 ± 1	365 ± 3	150 ± 2	360 ± 3	94 ± 2	355 ± 3	32 ± 1	300 ± 5
T380 M0	360	0	60	370 ± 3	2 ± 1	384 ± 3	140 ± 2	380 ± 3	88 ± 2	376 ± 3	18 ± 1	300 ± 5
T380 M3	380	3	60	370 ± 3	2 ± 1	384 ± 3	139 ± 2	380 ± 3	88 ± 2	376 ± 3	17 ± 1	300 ± 5
T380 M7	380	7	60	375 ± 3	2 ± 1	384 ± 3	137 ± 2	380 ± 3	86 ± 2	376 ± 3	15 ± 1	300 ± 5
T390 M0	390	0	60	385 ± 3	2 ± 1	392 ± 3	130 ± 2	390 ± 3	85 ± 2	385 ± 3	13 ± 1	304 ± 5
T390 M3	390	3	60	385 ± 3	2 ± 1	392 ± 3	130 ± 2	390 ± 3	84 ± 2	385 ± 3	13 ± 1	306 ± 5
T390 M7	390	7	60	385 ± 3	2 ± 1	392 ± 3	127 ± 2	390 ± 3	81 ± 2	383 ± 3	11 ± 1	306 ± 5



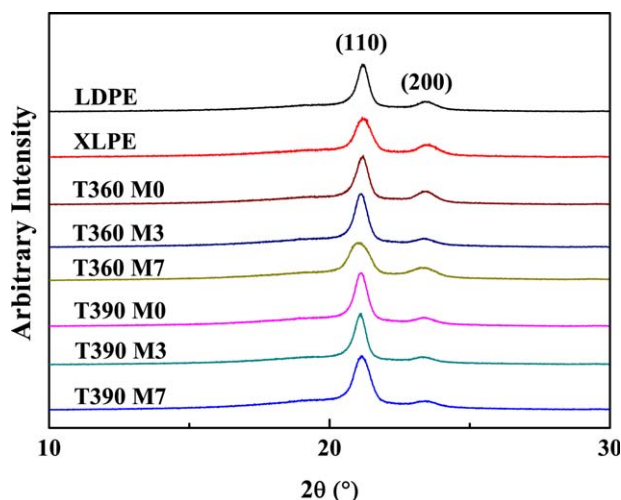
**Figure 2.** Gel contents of decrosslinked XLPE samples treated with supercritical methanol at various reaction temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

360°C, 380°C, and 390°C, were 31.0%, 21.8%, and 5.1%, respectively. At the methanol feeding rate of 7 mL/min, the gel fraction values for T360M7, T380M7, and T390M7 products (processed at 360°C, 380°C, and 390°C) were 20.6%, 15.2%, and 0%, respectively. As a result, XLPE was fully decrosslinked and converted into thermoplastic PE at the methanol feeding rate of 7 mL/min and 390°C in the extruder. The observation indicates that XLPE is basically decrosslinked because of thermal dissociation of the C–C bonding and the supercritical methanol conditions accelerate the decrosslinking reaction. These results are well in agreement with those reported from the batch reaction.<sup>19–25</sup> However, the continuous supercritical extrusion process resulted in lower degree of decrosslinking effect than that of the batch type reactor.<sup>23</sup>

This difference between batch and continuous reactors can be attributed to two reaction parameters: smaller methanol content



**Figure 3.** FT-IR spectra of neat LDPE, XLPE, and decrosslinked XLPEs treated with supercritical methanol at various reaction temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** XRD curves of neat LDPE, XLPE, and decrosslinked XLPEs treated with supercritical methanol at various reaction temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and shorter residence time in extruder. In the continuous extrusion process, maximum methanol feeding rate was limited to 7 mL/min because above this feeding rate severe vent-up of resin occurred through the gas vent. The reaction time is determined by the retention time of sample inside extruder. The retention time was also limited to shorter than 2 min because of the restrictions in length of the extruder. That is, the efficiency of the continuous supercritical decrosslinking in extruder is expected to be improved through the design of an extruder capable of accepting greater methanol feeding rate and providing longer retention time.

### Structural Analysis of Decrosslinked XLPE

**Chemical Structure.** Figure 3 shows the FT-IR spectra of decrosslinked XLPE, XLPE, and neat LDPE. Every sample represents a peak at 2800–3000  $\text{cm}^{-1}$ , indicating  $\text{sp}^3$  C–H stretching mode, and a peak at 1470  $\text{cm}^{-1}$ , indicating C–H bending mode.<sup>23,29</sup> The results, which does not show  $\text{sp}^2$  C–H (3000–3300  $\text{cm}^{-1}$ ),  $\text{sp}$  C–H (>3,300  $\text{cm}^{-1}$ ), and C=C (1600–1650  $\text{cm}^{-1}$ ) peaks, represent that a double or a triple bond were not formed.<sup>25,30</sup> Oxidation peaks, such as CO (900–1,300  $\text{cm}^{-1}$ ) and C=O (1,600–1,800  $\text{cm}^{-1}$ ), were not observed, indicating that any other side reactions do not occur except decrosslinking reaction.<sup>24,25,31</sup> The results signify that the chemical structure of PE did not change in spite of supercritical decrosslinking reaction.

**Crystallographic Structure.** The XRD patterns of decrosslinked XLPE products, XLPE and neat LDPE are shown in Figure 4. Each sample revealed three characteristic scattering peaks of (110) and (200) plane, representing the orthorhombic unit cell of PE, and a broad amorphous halo from the amorphous portions of polymer.<sup>21,24</sup> According to these results, the XLPE and decrosslinked XLPE products are considered to have very similar crystalline structure as neat LDPE. Through the comparison of the quantitative areas of peaks, the crystallinity values ( $X_{c,xrd}$ )

**Table II.** Characterizations of Crystallinity and Viscoelasticity of Neat LDPE, XLPE, and the Decrosslinked XLPEs

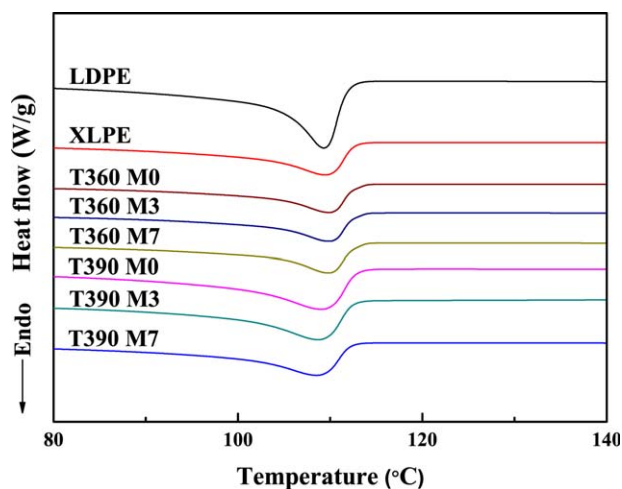
Sample	$X_{c,XRD}$	$X_{c,DSC}$	Terminal slope	
			$G'$	$G''$
LDPE	0.44	0.34	0.67	0.50
XLPE	0.36	0.33	NA	NA
T360 M0	0.37	0.36	0.27	0.23
T360 M3	0.38	0.37	0.29	0.24
T360 M7	0.38	0.38	0.30	0.28
T380 M0	0.40	0.42	0.41	0.36
T380 M3	0.42	0.36	0.42	0.39
T380 M7	0.40	0.35	0.49	0.45
T390 M0	0.39	0.40	0.6	0.45
T390 M3	0.41	0.37	0.65	0.49
T390 M7	0.41	0.44	0.73	0.56

\*NA, not available.

from XRD data (listed in Table II) were calculated using the following equation:

$$X_{c,xrd} = (I(110) + I(200)) / I_{total} \quad (2)$$

where  $I(110)$  and  $I(200)$  are the intensity values of (110) and (200) reflections, respectively, and  $I_{total}$  is the total intensity. The decrosslinked XLPE showed crystallinity value of approximately 40%, comparable with that of LDPE. The crystallinity was observed as independent of the degree of crosslinking. Based on the results of the FT-IR spectrometry and XRD examinations, the decrosslinked XLPE has the same chemical and crystallographic structure as neat LDPE and supercritical methanol does not substantially affect the chemical and crystallographic structures of the decrosslinked products.



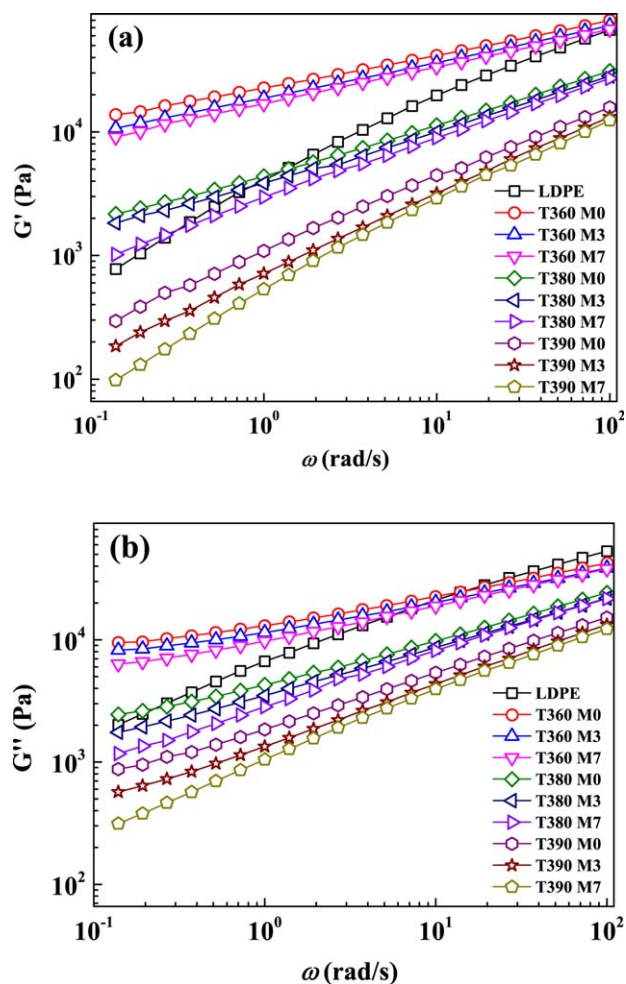
**Figure 5.** DSC thermograms of neat LDPE, XLPE, and decrosslinked XLPEs treated with supercritical methanol at various reaction temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Thermalcaloric Behavior

Figure 5 shows DSC thermographs of neat LDPE, XLPE, and decrosslinked XLPE treated at various supercritical reaction conditions. All curves were obtained from the second heating at a heating rate of 10°C/min to get melting temperature without thermal hysteresis. They revealed one endothermic melting peak at 109°C, indicating a unimodal lamella close to that of neat LDPE. The crystallinity values obtained from DSC ( $X_{c,DSC}$ , Table II) were calculated using the following equation:

$$X_{c,DSC} = \Delta H_m / \Delta H_{m,LDPE} \quad (3)$$

where,  $\Delta H_{m,LDPE} = 285$  J/g is the theoretical heat of fusion of perfect crystal of LDPE.<sup>32</sup> The decrosslinked XLPE, XLPE and neat LDPE revealed almost the same crystallinity of  $X_{c,DSC} = 0.4$ . The  $X_{c,DSC}$  value was consistent with  $X_{c,xrd}$  value determined from XRD examinations. The thermal analyses results indicate that the decrosslinked XLPE experienced the same crystal melting behavior and crystallinity as the neat LDPE.



**Figure 6.** (a) Storage moduli ( $G'$ ) and (b) loss moduli ( $G''$ ) of neat LDPE and decrosslinked XLPEs treated with supercritical methanol at various reaction temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Viscoelastic Behavior

Figure 6 shows the dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) curves of molten neat LDPE and decrosslinked XLPE at 180°C. The  $G'$  and  $G''$  values of decrosslinked XLPE samples were significantly affected not only by reaction temperature, but also by methanol content. The  $G'$  and  $G''$  values of the produced decrosslinked XLPE decreased with an increase in the reaction temperature and methanol content. The reduction in the  $G'$  and  $G''$  values with temperature and methanol was much larger at a low frequency than at a high frequency. The frequency dependence of  $G'$  and  $G''$  values in the crosslinked XLPE stems from the difference in the terminal slopes of  $G'$  and  $G''$  of the samples (Table II). The terminal slopes of  $G'$  and  $G''$  of crosslinked XLPEs diminished with a decrease in reaction temperature and methanol content. The slope change of  $G'$  was observed being more sensitive to the structure than that of  $G''$ . 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  $G'' \propto \omega$ .<sup>19,33</sup> The slope is very sensitive to the degree of crosslinking of polymer.<sup>19,21</sup> As the degree of crosslinking of polymer increases, the mobility of polymer chains is further restricted. The restriction of polymer chain dynamics enhances the solid-like elastic response, causing the nonterminal behavior in which terminal slope approaches zero. For example, modulus of ideal Hookean solid is independent of frequency and just proportional to the strain.<sup>34</sup> As a result, smaller values and steeper terminal slopes of  $G'$  and  $G''$  at high reaction temperature and larger methanol content verifies that the degree of crosslinking decreases with an increase in the reaction temperature and methanol content.

### CONCLUSIONS

The peroxide crosslinked PE was successfully decrosslinked through reaction in supercritical methanol in a continuous multiscale single screw extrusion process. Reaction temperature was set from 360°C to 390°C and the amount of methanol feeding was varied from 0 to 7 mL/min. The extruder ( $L/D = 36$ ,  $D = 40$  mm), with methanol injection pump, was kept in the supercritical conditions of methanol during extrusion. The gel content value decreased with an increase in the reaction temperature and methanol content. Although XLPE was in contact with supercritical methanol for shorter than 2 min retention time in the continuous supercritical extruder, it was successfully decrosslinked at the methanol feeding rate of 7 mL/min and above 390°C. The decrosslinking efficiency of the continuous supercritical extruder is expected to be improved through the optimization of extruder design to accept further methanol feeding rate and provide longer retention time.

### ACKNOWLEDGMENTS

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