**RHEOLOGICAL AND PHYSICAL PROPERTIES OF DECROSS-LINKED POLYETHYLENE FOAMS USING EXTRUDER**

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1. Introduction
Recycling of thermosetting polymers such as crosslinked polyethylene have been taken a great attention because of deep consideration of prevention of environmental pollution and of resource conservation over the world. However, even this moment, most industrial wastes of crosslinked polymers are burned as fuel or disposed of in landfills because they are difficult to process into other useful material due to their low fluidity and poor moldability. Although there are some ways to recycle the waste XLPE such as thermal recycling, thermal decomposition and blending, these methods are not economical compared with material recycling. In this report, we investigated a thermoplasticization method to recycle irradiation-crosslinked polyethylene foam by using a continuous supercritical single screw extruder and reported the relationships between the rheological and physical properties of the decross-linked polyethylene.

In addition, chemical kinetics for the decross-linking reaction is proposed based on the gel concentration and reaction temperature.

2. Experimental
Linear polyethylene (raw PE) and crosslinked polyethylene (XLPE) foam with 35~65% gel fraction were supplied from Youngbo Chemical in Korea. XLPE were manufactured from the raw PE by using irradiation-induced crosslinking. Methanol (MeOH) (99.5%, Sanchun Chemical) were used as supercritical media and xylene(Sigma-Aldrich, Inc.) as a solvent for extraction of de-crosslinked XLPE. Decross-linked reaction was performed using a single multi staged screw extruder(L/D=36, D=40mm). The degree of cross-linking, molecular weight and thermal properties of products were analyzed using GPC (Gel Permeation Chromatography), DSC (Differential scanning calorimeter), TGA (Thermogravimetric Analysis), and FTIR (Fourier-Transformation Infrared). Observations of phase morphology were performed using SEM(Scanning Electron Microscopy). All specimens were manufactured by Injection Molding machine. Measurements of physical properties of specimens were carried out by Impact Tester, Instron Tensile Tester and TMA(Thermal Mechanical Analyzer).

3. Results and Discussion
Figure 1 shows temperature dependence of gel content of XLPE after supercritical MeOH treatment. Reaction time was 5 min for each run and original XLPE had 65% gel fraction. Gel content shows slow decrease up to 350°C and sharp down above 360°C as temperature increases. Gel-free polyethylene was achieved above 380°C, indicating that XLPE was completely thermoplasticized by supercritical MeOH treatment above 380°C.

![Figure 1. Gel content of XLPE after supercritical MeOH treatment at various reaction temperatures.](image-url)
Table 1 shows molecular weight of the thermoplasticized XLPE by supercritical MeOH at various temperatures. Molecular weight is measuring by using the extracted from the treated XLPE by hot xylene. Molecular weight of the extracted decreases with temperature. Especially, the extracted from the treated XLPE containing 26% gel, has lower molecular weight and broader molecular weight distribution than raw PE. This indicates that chain decomposition takes place at random site, not at the selective crosslinking junctions.

Table 1. Characterizations of raw PE and XLPEs after supercritical MeOH treatment at various temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Gel content (%)</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Mw</td>
</tr>
<tr>
<td>360</td>
<td>22,000</td>
<td>277,000</td>
</tr>
<tr>
<td>380</td>
<td>15,000</td>
<td>201,000</td>
</tr>
<tr>
<td>400</td>
<td>11,000</td>
<td>74,000</td>
</tr>
<tr>
<td>Raw LDPE</td>
<td>40,000</td>
<td>343,000</td>
</tr>
</tbody>
</table>

Figure 2 shows FT-IR spectra of raw PE and XLPEs and the treated XLPEs at various temperatures.

Figure 3 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 1. In Figure 4a, 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 4b, 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, \( \Delta H_m \), using the following equation:

\[
X_{c,DSC} = \Delta H_m / \Delta H_{m,PE}
\]

where \( \Delta H_{m,PE} = 277 \) J/g was the theoretical heat of fusion of perfect crystalline high density polyethylene.\(^1\) The decrosslinked had the almost same crystallinity about \( X_{c,DSC} = 0.5 \) as LDPE.
Figure 3. DSC thermographs of LDPE and the decrosslinked XLPEs (A) at cooling scan and (b) heating scan.

Figure 4 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 equation 2:

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

, 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 equation 3 and orthorhombic plane distance relationship in equation 4.

$$d_{hkl} = \frac{\lambda}{2\sin \theta_{hkl}}$$

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

All WAXS results were also summarized in Table 1. LDPE had orthorhombic lattice dimensions of $a=7.39\,\text{Å}$, $b=4.97\,\text{Å}$ 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 4. WAXS patterns of LDPE and the decrosslinked XLPEs at various temperatures.

Figure 5 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. 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 density. The amorphous polyethylene is well known to have very low beta or gamma glass transition less than 100°C. 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.

![Figure 5. Storage moduli (E’) of LDPE and the decrosslinked XLPEs.](image)

Figure 5 shows tensile strength and impact energy of treated XLPE. XLPE foam was not tested because it was impossible to mold a specimen for mechanical tests. Tensile strength and impact energy of the treated XLPE gradually decreases with increase in reaction temperature. Because gel fraction and molecular weight of the treated decreases with temperature as shown in Figure 2 and Table 1. However, the thermoplasticized polyethylene at 360°C has mechanical properties comparable with raw polyethylene.

![Figure 6. (a) Tensile strength and (b) impact energy of XLPE after supercritical MeOH treatment.](image)

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References