

Effect of Solvents on De-Cross-Linking of Cross-Linked Polyethylene under Subcritical and Supercritical Conditions

Hong-shik Lee,[†] Ju Hyeong Jeong,[‡] Giyoung Hong,[‡] Hang-Kyu Cho,[§] Bum Ki Baek,^{||} Chong Min Koo,^{||} Soon Man Hong,^{||} Jaehoon Kim,^{⊥,⊗} and Youn-Woo Lee^{*,‡}

[†]Clean Energy Research Center, Korea Institute of Science and Technology, Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

[‡]School of Chemical and Biological Engineering and Institute of Chemical Processes, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea

[§]Department of Chemical and Biomolecular Engineering, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 121-742, Republic of Korea

^{||}Nanohybrids Research Center, Korea Institute of Science and Technology, Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

[⊥]School of Mechanical Engineering, Sungkyunkwan University, 2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea

[⊗]Sungkyun Advanced Institute of Nano Technology (SAINT), 2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea

S Supporting Information

ABSTRACT: The effect of various solvents on the de-cross-linking reaction of cross-linked polyethylene under subcritical and supercritical conditions was studied. The gel content of the de-cross-linked polyethylene decreased from 60 to 0.8–2.5% at 380 °C within 5 min in all of the solvents tested in this study. When water, ethanol, and 2-propanol were used, the M_w of the de-cross-linked polyethylenes decreased from 349,000 to 200,000–227,000 g/mol, and much lower M_w values of 70,000–90,000 g/mol were observed when acetone and diisopropyl ether were used. The de-cross-linked polyethylenes treated in the different solvents had a very similar chemical structure to raw polyethylene. According to a kinetic study using a first-order reaction model, the de-cross-linking rate in each solvent increased in the order 2-propanol < ethanol < *n*-hexane < water < methanol << diisopropyl ether << acetone at 350 °C.

1. INTRODUCTION

Plastics have been extensively used in various industrial fields due to their unique advantages such as light weight, low cost, excellent insulating ability against heat and electricity, convenience of maintenance and repair, and degradation resistance. In addition, the properties of plastic materials can easily be controlled using various types of additives. However, because of the large-scale use of plastics, a substantial amount of plastic waste is generated, which has become an increasingly serious social and economic problem related to limited resources and the environment. Although landfills and incineration are the most common ways to treat plastic wastes, these two methods are not considered ideal solutions. The space for landfills is limited, landfill costs are becoming expensive, and breakdown products can cause soil contamination. Incineration often produces highly toxic gases, which cause serious air pollution. Therefore, there is great need for the development of more sustainable, less toxic, and recyclable alternatives to the traditional methods for treating plastic waste.

Thermosetting resins are regarded as very recalcitrant materials in the view of waste treatment because they are insoluble and infusible due to their cross-linked structure. A great deal of effort has been directed to the development of recycling techniques for thermosetting resins. This includes the

recovery of energy by incineration (thermal recycling), blending with other materials after grinding (physical recycling), and depolymerization/de-cross-linking (chemical recycling).^{1–3} Despite these efforts, the recycling of thermosetting resin remains a great challenge, and there is an urgent need to develop an appropriate method.

A supercritical fluid is defined as a substance that exists at above its critical pressure and temperature. Supercritical fluids have the advantages of both gas and liquid, that is, the high permeability of gas and the high density of liquid. These characteristics make supercritical fluid an excellent alternative solvent for toxic materials in various applications. In addition, the properties of supercritical fluids such as density, polarity, solubility, and thermal conductivity can be controlled by adjusting the pressure and temperature. In the area of plastic recycling, supercritical fluids hold great promise as a medium and as a reactant.^{4–17} It has been reported that the recycling of condensation polymers can be achieved via depolymerization using supercritical solvents such as water and methanol.^{6–13}

Received: February 26, 2013

Revised: April 3, 2013

Accepted: April 24, 2013

Published: April 24, 2013

These solvents can participate in hydrolysis or solvolysis reactions to induce the reverse reaction of condensation. For example, several groups reported that polyethylene terephthalate could be depolymerized in supercritical water⁶ and methanol.^{7–9} Piñero et al. reported that dimethyl carbonate and bisphenol A were obtained via depolymerization of polycarbonate using supercritical methanol and NaOH.¹⁰ However, the role of supercritical solvents in recycling of addition polymers such as cross-linked polyethylene (XLPE) has not been known well, although some studies already have shown that recycling of addition polymers is possible using supercritical water or alcohols.^{14–17}

XLPE is one of the most widely used thermosetting resins because of its good insulation properties against heat and electricity compared to its non-cross-linked counterpart. Previously, several researchers have proposed using supercritical fluids to de-cross-link XLPE. According to Goto et al., silane-cross-linked polyethylene (S-XLPE) can be de-cross-linked completely in supercritical water and alcohols. They noted that the temperature required for de-cross-linking was lower in supercritical alcohol than in supercritical water.^{14,15} This implies that the de-cross-linking reaction of S-XLPE was dependent on the supercritical solvents used. The structure of S-XLPE is different from those of other XLPEs such as peroxide-cross-linked polyethylene (P-XLPE) and radiation-cross-linked polyethylene (R-XLPE). The cross-linking bonds of S-XLPE consist of a siloxane group, whereas the cross-linking bonds of P-XLPE and R-XLPE consist of a C–C bond. Therefore, the de-cross-linking mechanism of P-XLPE and R-XLPE is considered to be different from that of S-XLPE. Even though supercritical solvents have clear advantages over other methods for recycling of P-XLPE and R-XLPE, only a few studies have been published.^{16–18} For example, Watanabe et al.¹⁶ and Lee et al.¹⁷ studied the de-cross-linking of P-XLPE in supercritical water and the de-cross-linking of R-XLPE in supercritical methanol, respectively. However, a systematic study on the effect of solvents in the de-cross-linking of P-XLPE or R-XLPE has not been reported yet.

In this study, the effect of various sub- and supercritical solvents on the de-cross-linking of R-XLPE was investigated. The solvents examined include subcritical water (SUBW; $T_c = 374.0\text{ }^\circ\text{C}$, $P_c = 22.1\text{ MPa}$), supercritical methanol (SCM; $T_c = 239.5\text{ }^\circ\text{C}$, $P_c = 8.1\text{ MPa}$), supercritical ethanol (SCE; $T_c = 240.8\text{ }^\circ\text{C}$, $P_c = 6.1\text{ MPa}$), supercritical 2-propanol (SCPA; $T_c = 235.2\text{ }^\circ\text{C}$, $P_c = 4.7\text{ MPa}$), supercritical *n*-hexane (SCH; $T_c = 234.5\text{ }^\circ\text{C}$, $P_c = 3.0\text{ MPa}$), supercritical acetone (SCA; $T_c = 235.0\text{ }^\circ\text{C}$, $P_c = 4.7\text{ MPa}$), and supercritical isopropyl ether (SCPE; $T_c = 227.2\text{ }^\circ\text{C}$, $P_c = 28.3\text{ MPa}$). The effects of different sub- and supercritical fluids on the properties of de-cross-linked XLPE including molecular weights, molecular weight distributions, chemical compositions, crystalline structure, and melting points are discussed in detail. Lastly, the de-cross-linking rate in each solvent is discussed using a first-order reaction model.

2. EXPERIMENTAL SECTION

2.1. Materials. XLPE foam with a gel content of 60% was obtained from Youngbo Chemical Co., Ltd., Korea. XLPE was manufactured from low-density polyethylene ($M_w = 349,000\text{ g/mol}$, polydispersity index (PDI) = 7.0, LG Chem., Ltd., Korea) by the peroxide cross-linking method using dicumyl peroxide. As reaction solvents, methanol (99.5%), ethanol (99.5%), 2-propanol (99.5%), *n*-hexane (HPLC grade), acetone (99.5%), and isopropyl ether (99.0%) were purchased from Samchun

Pure Chemical Co., Ltd. (Korea) and used without further purification. Water obtained from a water purification apparatus (Milli-Q Advantage A10, Millipore Co., Ltd.) was used. Xylenes (ACS reagent, Sigma-Aldrich, Inc.) and a commercial antioxidant (Irganox 101, Ciba, USA) were used to measure the gel content of XLPE and the treated samples.

2.2. Apparatus. De-cross-linking experiments were carried out using a batch reactor system. The reactor schematic is shown in Figure S1 (see the Supporting Information). The reactors were made of stainless steel (grade 316) with a volume of 40 cm^3 . A molten salt bath filled with a mixture of NaNO_3 , KNO_3 , and $\text{Ca}(\text{NO}_3)_2$ was used to heat the reactors. The temperature of the salt was measured with a K-type thermocouple probe dipped into the salt and regulated with a PID controller. Above the salt bath, a reciprocating-type shaker was installed to stir the reactants inside the reactors.

2.3. Procedure. First, a predetermined amount of XLPE and a solvent were introduced into the batch reactor. The amount of XLPE and solvent was calculated based on the density at an experimentally desired temperature and pressure. The reactor was then sealed tightly and immersed into the molten salt heated to a predetermined temperature. The material in the reactor was then stirred with the shaker for a predetermined time. Because it takes approximately 2 min to elevate the internal temperature of the reactor to the temperature of the salt, the reaction time was defined as the isothermal period after 2 min from the immersion of the reactor. After a predetermined time, the reactor was removed from the salt and cooled in water to stop the reaction. After cooling, the solid product in the reactor was separated from the solvent and dried in a vacuum oven to remove the residual solvent. The details of the experimental conditions are listed in Table S1 (see the Supporting Information).

2.4. Analysis. To quantify the degree of cross-linking of the samples, the gel contents of raw and treated samples were measured according to the method presented in ASTM D2765-01 (2006). The weighed sample was extracted in boiling xylenes containing antioxidants over 12 h and dried to remove residual xylenes. The weight of the sample was measured to estimate the gel content using the following equation:

$$\begin{aligned} \text{gel content (\%)} &= [\text{wt of sample after extraction (mg)} \\ &\quad / \text{wt of sample before extraction (mg)}] \\ &\quad \times 100 \end{aligned} \quad (1)$$

The molecular weight was measured using high-temperature gel permeation chromatography (GPC 150, Waters Corp., USA). The specimen was dissolved in trichlorobenzene containing 0.01% of butylated hydroxytoluene at $160\text{ }^\circ\text{C}$ for 4 h and injected into the GPC containing a MIXED-B column.

A differential scanning calorimeter (DSC, Q200, TA Instrument Inc., USA) was used to measure the melting temperature (T_m). The chemical structure of the samples was analyzed using a Fourier transform infrared spectrophotometer (FT-IR, Nicolet 6700, Thermo Scientific Inc., USA), and the crystalline structure was measured using an X-ray diffractometer (XRD, D-MAX2500-PC, Rigaku Co., Japan).

3. RESULTS AND DISCUSSION

3.1. Properties of DXPE in Various Solvents. **3.1.1. Gel Content and Molecular Weight.** Table 1 lists the gel contents and molecular weights of de-cross-linked polyethylenes

Table 1. Gel Contents and Molecular Weights of PE and DXPEs Treated in the Various Sub- and Supercritical Solvents at 380 °C for 5 min

		gel content (%)	M_n (g/mol)	M_w (g/mol)	PDI
PE		0	40,000	349,000	7.0
XLPE		60	NA ^a	NA	NA
DXPE	SUBW	1.3	16,000	206,000	12.7
	SCM	1.3	16,000	172,000	10.7
	SCE	2.5	18,000	215,000	11.8
	SCPA	1.9	21,000	227,000	11.0
	SCH	1.8	16,000	154,000	9.5
	SCA	1.3	13,000	91,000	7.0
	SCPE	0.8	12,000	73,000	6.0

^aNA, not available.

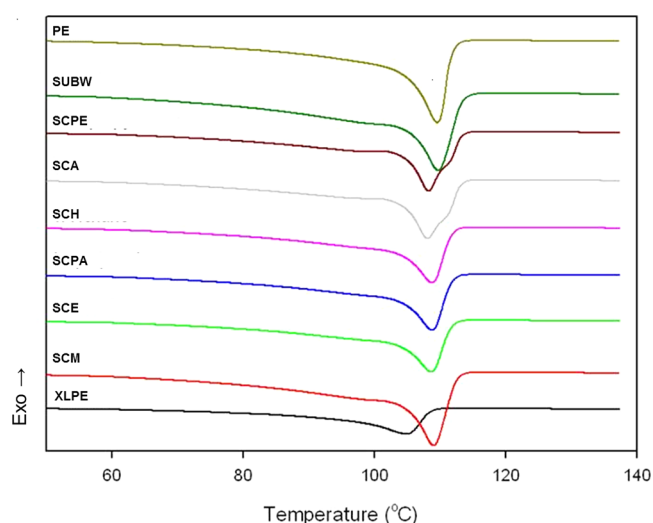
(DXPEs) treated with the various sub- and supercritical solvents at a fixed temperature of 380 °C. The gel content decreased significantly from 60 to <2.5%. This indicates that almost complete de-cross-linking of the XLPE can occur in the solvents tested in this study. The molecular weights of DXPEs are lower than that of the base resin used for producing XLPE. When SUBW, SCE, and SCPA were used, the M_w values were 200,000–227,000 g/mol, whereas much lower M_w values of 70,000–90,000 g/mol were observed when SCA and SCPE were used. The PDI values of DXPEs were larger than that of PE, except for the DXPEs produced from SCA and SCPE.

The decrease in molecular weight and increase in PDI indicate that the backbone chains of XLPE as well as the cross-linking bonds were dissociated during the de-cross-linking reaction. However, compared with the dissociation of the cross-linking bonds, the dissociation of the backbone chains did not seem to be significant; that is, the extent of change in the molecular weight and polydispersity was not large. For example, in the case of SUBW, the molecular weight of DXPE was more than half that of PE, whereas the cross-linking bonds were almost dissociated. On the basis of these results, it can be concluded that the de-cross-linking reaction was selective to some degree toward the cross-linking bonds. This is probably due to the difference in the radical stability between the secondary carbons in backbone chains and the tertiary or quaternary carbons in cross-linking bonds, as discussed in our previous study.¹⁷ When SCA and SCPE were used, the

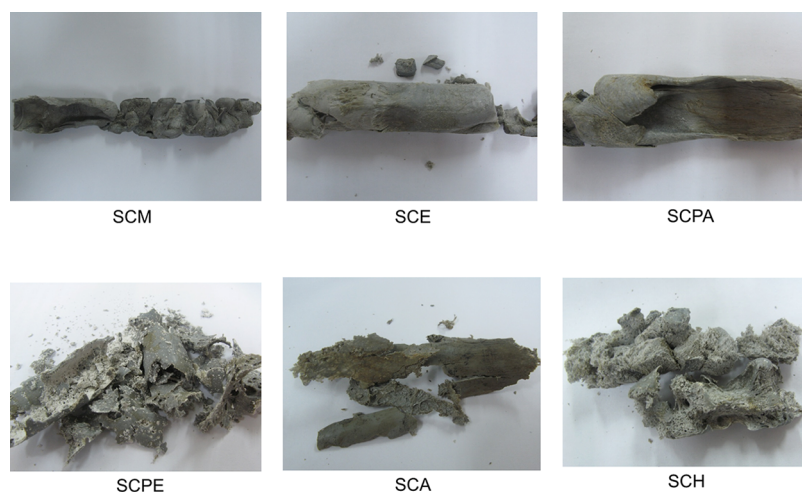
dissociation reaction of the backbone chain was more activated than that in the other solvents, which resulted in the formation of species with lower molecular weight.

3.1.2. External Appearance. The external appearances of DXPEs produced with the different sub- and supercritical fluids are presented in Figure 1. All products had a cylindrical shape or the shape of broken parts of a cylinder, which resembled the inner shape of the reactor. This suggests that polymer had melted and filled in the reactor during the reaction, which provides further evidence of complete de-cross-linking. The DXPEs treated in SCA and SCPE were very brittle, whereas the other DXPEs were slightly elastic. This is probably due to the much lower molecular weight of DXPEs treated with SCA and SCPE, which would decrease the elasticity.

3.1.3. Thermal Behavior. The melting temperatures of PE, XLPE, and DXPEs treated in the different solvents were measured by DSC. The thermographs of the heating period are shown in Figure 2. Because the gel content of XLPE used in

**Figure 2.** DSC curves of PE, XLPE, and DXPEs treated in the various sub- and supercritical solvents at 380 °C for 5 min.

this study was 60%, some portion of un-cross-linked polyethylene was present in XLPE. Therefore, the measured T_m of

**Figure 1.** External appearance of DXPE products treated in the various sub- and supercritical solvents at 380 °C for 5 min.

XLPE corresponded to un-cross-linked polyethylene. The T_m values of PE and XLPE were 109.6 and 104.8 °C, respectively. This means that the PE was more prone to be crystallized compared with the un-cross-linked PE in XLPE. This can be explained by the difference in the molecular weight distribution. Because the cross-linking reaction can occur on any carbon in the PE chains, the probability that a PE chain is cross-linked is dependent on the number of carbons in the chain, which corresponds to the molecular weight of the chain. Therefore, the long PE chains are more likely to be cross-linked, whereas the short PE chains are not. Thus, the average molecular weight of the un-cross-linked PE in XLPE was expected to be lower than that of PE; that is, the un-cross-linked PE in XLPE would be more easily crystallized compared with PE.

The T_m values of the DXPEs were very similar to that of PE. However, a closer inspection revealed that the T_m values were slightly decreased except for the SUBW case. It is not clear what is causing the slight change in T_m , but the change in molecular weight and chemical structure may be responsible for the change in T_m . The decreased molecular weight of DXPEs can cause a decrease in T_m . In contrast, the increase in T_m can occur if the chemical structure of the PE chain is changed during the de-cross-linking. If a side reaction occurs to form carbonyl group or epoxide group on a PE chain, these groups can enhance the intermolecular interaction. The chemical structure of DXPEs will be discussed in the next section.

3.2. Chemical Structure of DXPEs. Figure 3 shows the FT-IR spectra of PE, XLPE, and DXPEs. The strong peaks at

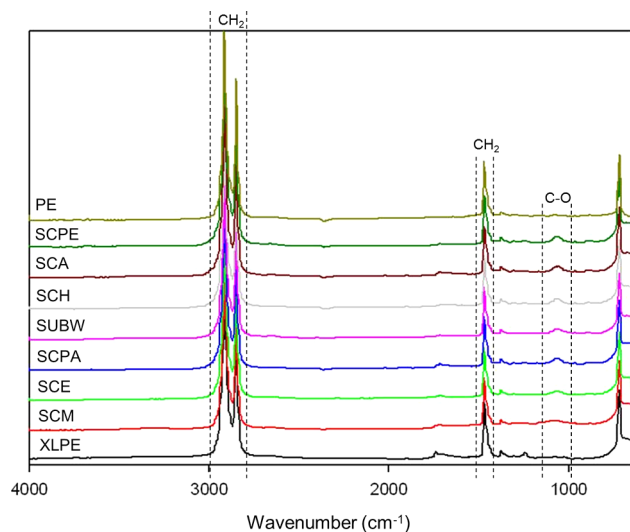


Figure 3. FT-IR spectra of PE, XLPE, and DXPEs treated in the various sub- and supercritical solvents at 380 °C for 5 min.

2925 and 2850 cm^{-1} correspond to the sp^3 C–H stretching mode, and the peak at 1470 cm^{-1} corresponds to the C–H bending mode. In the spectra of DXPEs, a weak peak was observed near 1100 cm^{-1} , which corresponds to the C–O bond. The presence of the C–O bond indicates that oxidation of the PE chain occurred during the de-cross-linking reaction. It is not clear what caused the oxygen incorporation into DXPEs, but it may have been due to oxygen molecules that were dissolved in the solvents or were present in the reactor. Because no significant difference among the solvents was observed in the FT-IR spectra and the oxidation occurred even when hexane with no oxygen atom was used, the oxygen atoms in the

solvent molecules may not be responsible for the oxygen incorporation.

The XRD patterns of PE, XLPE, and DXPEs are shown in Figure 4. The scattering peaks of the (110) and (200) plane

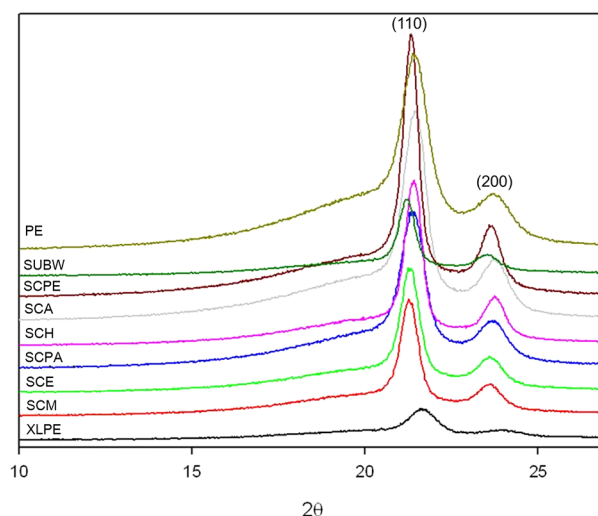


Figure 4. XRD patterns of PE, XLPE, and DXPEs treated in the various sub- and supercritical solvents at 380 °C for 5 min.

representing the orthorhombic unit cell of polyethylene¹⁸ were observed in the samples. According to this result, the DXPEs were considered to have a crystalline structure very similar to that of raw PE. On the basis of the results of the FT-IR and XRD analyses, the DXPE treated in different sub- and supercritical fluids had a chemical structure very similar to that of raw PE, and the solvent did not affect significantly the structure of the de-cross-linked products.

3.3. De-Cross-Linking Rate in Various Sub- and Supercritical Fluids. The effects of reaction time on the gel content at 350 °C in the sub- and supercritical solvents are presented in Figure 5. Among the alcohols tested, the decrease in gel content was fastest in SCM and became slower as the number of carbons increased. Compared with the other solvents, the decrease in gel content was remarkably fast in SCA and SCPE. The much higher chain scission reactivity of SCA and SCPE may also be responsible for the low molecular weight of de-cross-linked products.

The rate constant of de-cross-linking in each solvent was calculated using a first-order model as described in our previous study.¹⁷ In this model, it was assumed that the de-cross-linking rate was linearly dependent on the gel concentration C_{gel} , which is defined in the following equation:

$$\text{gel concn (g/cm}^3\text{)} = \frac{\text{gel content (\%)}}{100} \times \frac{\text{wt of polymer (g)}}{\text{vol of reactor (cm}^3\text{)}} \quad (2)$$

Under an assumption that the concentration of the solvent does not affect the reaction rate, the rate of disappearance of the gel is

$$\frac{dC_{\text{gel}}}{dt} = -kC_{\text{gel}} \quad (3)$$

where t is reaction time (min) and k is a rate constant (min^{-1}). Integration of this equation gives

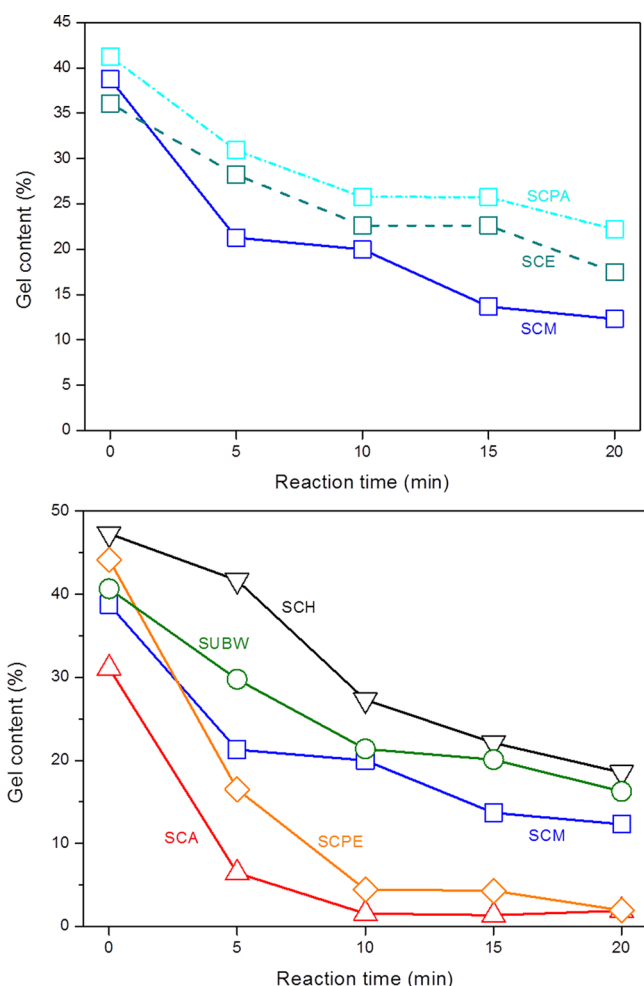


Figure 5. Change of gel content in the various sub- and supercritical solvents at 350 °C.

$$C_{\text{gel}} = C_{\text{gel},0} e^{-kt} \quad (4)$$

where $C_{\text{gel},0}$ is the initial gel concentration (g/cm^3).

Table 2 shows the rate constants in the sub- and supercritical solvents calculated with the least-squares method. The rate

Table 2. Rate Constant of De-Cross-Linking in the Various Sub- and Supercritical Solvents at 350 °C

solvent	rate constant (min^{-1})	solvent	rate constant (min^{-1})
SUBW	0.0513 ± 0.0039	SCH	0.0476 ± 0.0044
SCM	0.0696 ± 0.0087	SCA	0.3071 ± 0.0287
SCE	0.0380 ± 0.0033	SCPE	0.1981 ± 0.0132
SCPA	0.0351 ± 0.0040		

constants in SCA and SCPE were an order of magnitude larger than those in the other solvents. In the other solvents, the rate constant was in the order $\text{SCM} > \text{SUBW} > \text{SCH} > \text{SCE} > \text{SCPA}$, but the differences were not significant. Generally, the polarity of solvent is one of the most dominant properties affecting a reaction behavior. However, except for a limited number of solvents,^{19–21} it is difficult to find the polarity values of solvents in their supercritical state. Nevertheless, several suppositions can be drawn from the de-cross-linking results. Because of its similar structure to that of PE, hexane is expected to have the strongest affinity with PE among the solvents used

in this study. However, the rate constant in SCH was not high when compared to SCM, SUBW, SCA, and SCPE. In addition, at the given reaction conditions, the dielectric constant of SUBW is around 14²⁰ and that of SCM is <7 .¹⁹ Despite the difference in the dielectric constants, the rate constants in these two solvents are very similar, as listed in Table 2. This may imply that the affinity between solvent and PE chain does not have a significant effect on the reaction rate, that is, the solvation mechanism is not significant during the de-cross-linking reaction. Therefore, high rate constants in SCA and SCPE may be caused by factors other than the polarity of the solvent. As is well-known, the diisopropyl ether is apt to be oxidized to form peroxide even at room temperature.²² Thus, the peroxide contained in the solvent as an impurity or formed by the reaction with oxygen inside the reactor can affect the de-cross-linking reaction. If the unstable peroxide is decomposed to form radicals, it can accelerate the radical formation on the PE chains and consequently increase the reaction rate. This explanation can be applied to the high reaction constant in SCA because acetone is easily changed to peroxide.²²

In view of the reaction rate, SCA and SCPE are the best solvents among the various sub- and supercritical solvents examined in this study. However, the de-cross-linking reactions in SCA and SCPE also cause a significant decrease in molecular weights of PE. It would be difficult to control de-cross-linking and chain scission due to the rapid radical reaction. There was no significant difference among the reaction rates and chemical structures using the other solvents; thus, other factors such as cost and environmental effect can be more important criteria for the selection of solvent in the de-cross-linking of XLPE.

4. CONCLUSION

In this work, the effect of various solvents on the de-cross-linking of XLPE under sub- and supercritical conditions was evaluated. The rate constant in each solvent was obtained using a first-order rate equation. The effect of different solvents on the chemical structure of the DXPE was found to be marginal. The de-cross-linking rate was an order of magnitude higher in supercritical acetone and supercritical isopropyl ether compared to those in other solvents. The fast reaction in supercritical acetone and supercritical isopropyl ether may also cause a significant decrease in the molecular weight of DXPE. Therefore, the conditions for de-cross-linking reaction need be optimized to minimize the decrease in molecular weight, which is important for efficient recycling.

■ ASSOCIATED CONTENT

Supporting Information

Figure S1, schematic diagram of a batch reactor system; Tables S1, experimental conditions for de-cross-linking of XLPEs in the various sub- and supercritical solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +82 2 880 1883. Fax: +82 2 883 9124. E-mail: ywlee@snu.ac.kr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment (Project 11-D24-OD).

■ REFERENCES

- (1) Fainleib, A.; Grigoyeva, O. *Recent Development in Polymer Recycling*; Transworld Research Network: Kerala, India, 2011.
- (2) Guo, J.; Guo, J.; Xu, Z. Recycling of non-metallic fractions from waste printed circuit boards: a review. *J. Hazard. Mater.* **2009**, *168*, 567.
- (3) Pickering, S. J. Recycling technologies for thermoset composite materials—current status. *Compos. Part A – Appl. Sci. Manuf.* **2006**, *37*, 1206.
- (4) Goto, M. Chemical recycling of plastics using sub- and supercritical fluids. *J. Supercrit. Fluids* **2009**, *47*, 500.
- (5) Goto, M.; Sasaki, M.; Hirose, T. Reactions of polymers in supercritical fluids for chemical recycling of waste plastics. *J. Mater. Sci.* **2006**, *41*, 1509.
- (6) Adschiri, T.; Sato, O.; Machida, K.; Saito, N.; Arai, K. Recovery of terephthalic acid by decomposition of PET in supercritical water. *Kagaku Kogaku Ronbunshu* **1997**, *23*, 505.
- (7) Genta, M.; Iwaya, T.; Sasaki, M.; Goto, M.; Hirose, T. Depolymerization mechanism of poly(ethylene terephthalate) in supercritical methanol. *Ind. Eng. Chem. Res.* **2005**, *44*, 3894.
- (8) Goto, M.; Koyamoto, H.; Kodama, A.; Hirose, T.; Nagaoka, S. Depolymerization of polyethylene terephthalate in supercritical methanol. *J. Phys.: Condens. Matter* **2002**, *14*, 11427.
- (9) Goto, M.; Koyamoto, H.; Kodama, A.; Hirose, T.; Nagaoka, S.; McCoy, B. J. Degradation kinetics of polyethylene terephthalate in supercritical methanol. *AIChE J.* **2002**, *48*, 136.
- (10) Piñero, R.; García, J.; Cocero, M. J. Chemical recycling of polycarbonate in a semi-continuous lab-plant. A green route with methanol and methanol-water mixtures. *Green Chem.* **2005**, *7*, 380.
- (11) Ozaki, J. I.; Djaja, S. K. I.; Oya, A. Chemical recycling of phenol resin by supercritical methanol. *Ind. Eng. Chem. Res.* **2000**, *39*, 245.
- (12) Okajima, I.; Yamada, K.; Sugeta, T.; Sako, T. Decomposition of epoxy resin and recycling of CFRP with sub- and supercritical water. *Kagaku Kogaku Ronbunshu* **2002**, *28*, 553.
- (13) Piñero-Hernanz, R.; Dodds, C.; Hyde, J.; García-Serna, J.; Poliakov, M.; Lester, E.; Cocero, M. J.; Kingman, S.; Pickering, S.; Wong, K. H. Chemical recycling of carbon fibre reinforced composites in nearcritical and supercritical water. *Compos. Part A – Appl. Sci. Manuf.* **2008**, *39*, 454.
- (14) Goto, T.; Yamazaki, T.; Sugeta, T.; Okajima, I.; Sako, T. Selective decomposition of the siloxane bond constituting the crosslinking element of silane-crosslinked polyethylene by supercritical alcohol. *J. Appl. Polym. Sci.* **2008**, *109*, 144.
- (15) Goto, T.; Yamazaki, T. Recycling of silane cross-linked polyethylene for insulation of cables using supercritical alcohol. *Hitachi Cable Rev.* **2004**, *23*, 24.
- (16) Watanabe, S.; Komura, K.; Nagaya, S.; Morita, H.; Nakamoto, T.; Hirai, S.; Aida, F. Development of cross-linked polymer material recycling technology by supercritical water. *Proceedings of the 7th International Conference on Properties and Applications of Dielectric Materials*; IEEE: Piscataway, NJ, 2003; p 595.
- (17) Lee, H.-s.; Jeong, J. H.; Cho, H. K.; Koo, C. M.; Hong, S. M.; Kim, H.; Lee, Y.-W. A kinetic study of the decross-linking of cross-linked polyethylene in supercritical methanol. *Polym. Degrad. Stab.* **2008**, *93*, 2084.
- (18) Cho, H.-K.; Hong, S. M.; Baek, K.-Y.; Koo, C. M.; Lee, H.-S.; Lee, Y.-W. Physical and rheological properties of thermoplasticized crosslinked-polyethylene foam in supercritical methanol. *Macromol. Res.* **2009**, *17*, 950.
- (19) Franck, E. U.; Deul, R. Dielectric behaviour of methanol and related polar fluids at high pressures and temperatures. *Faraday Discuss. Chem. Soc.* **1978**, *66*, 191.
- (20) Uematsu, M.; Franck, E. U. Static dielectric constant of water and steam. *J. Phys. Chem. Ref. Data.* **1980**, *9*, 1291.
- (21) Hiejima, Y.; Yao, M. Dielectric relaxation of lower alcohols in the whole fluid phase. *J. Chem. Phys.* **2003**, *119*, 7931.
- (22) Clark, D. E. *Peroxides and Peroxide Forming Compounds*. Ph.D. thesis, Texas A&M University, 2000.