

# Recycling of cross-linked polyolefin by decrosslinking reaction in supercritical fluid

Hong-shik Lee<sup>1</sup>, Ju Hyeong Jeong<sup>1</sup>, Hang-Kyu Cho<sup>2</sup>, Chong Min Koo<sup>2</sup>, Soon Man Hong<sup>2</sup>, Hwayong Kim<sup>1</sup>,  
Jaehoon Kim<sup>3</sup>, Youn-Woo Lee<sup>1\*</sup>

<sup>1</sup>School of Chemical and Biological Engineering & Institute of Chemical Processes, Seoul National University,  
599 Gwanak-ro, Gwanak-gu, Seoul 151-744 Korea

<sup>2</sup>Hybrid Materials Center, Korea Institute of Science and Technology,  
5 Wolsong-gil, Seongbuk-gu, Seoul 136-791 Korea

<sup>3</sup>Supercritical Fluid Research Laboratory, Energy and Environment Research Division,  
Korea Institute of Science and Technology,  
5 Wolsong-gil, Seongbuk-gu, Seoul 136-791 Korea

E-mail : [ywlee@snu.ac.kr](mailto:ywlee@snu.ac.kr), Fax : +82-2-883-9124

## INTRODUCTION

Cross-linked polyethylene (XLPE) has been used as an insulating material in various applications because of its excellent resistance against heat and electricity. However, because it is a thermosetting resin, it is very difficult to recycle XLPE. 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 [1-4]. Some researcher proposed the application of supercritical fluid as a tool for the recycling of thermosetting resin such as XLPE [5-7]. In this study, the recycling of XLPE by decrosslinking reaction in various supercritical fluids was investigated.

## MATERIALS AND METHODS

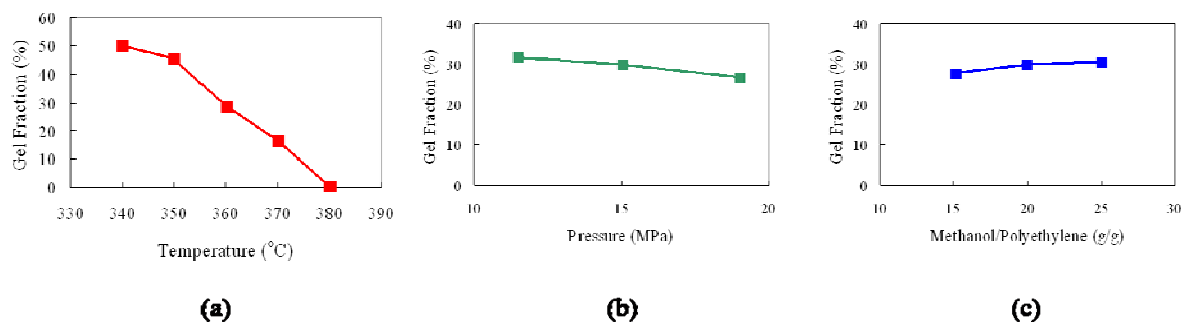
XLPE was supplied by Youngbo Chemicals Co. Ltd. (Korea) kindly. Methanol (99.5%, Samchun Pure Chemicals Co. Ltd., Korea), ethanol (94.5%, Samchun Pure Chemicals Co. Ltd., Korea), and 2-propanol (HPLC grade, Mallinckrodt Baker Inc.) were used as reaction solvents. Xylenes (99.0%, Samchun Pure Chemicals Co. Ltd., Korea) were used in the measurement of gel content.

The experiments were carried out using batch reactors. Reaction temperature was controlled by electric furnace and salt bath, and reaction pressure and weight ratio was determined by the amount of introduced reactants. After reaction, the residual solvent was dried in vacuum oven. The gel content of products was measured according to ASTM D 2765, and the molecular weight was measured by gel permeation chromatography. FT-IR spectroscopy was applied to investigate the structure of products, and the mechanical strength of products was measured.

## RESULTS

Figure 1 shows the effect several parameters on the decross-linking reaction of XLPE in supercritical methanol [7]. Reaction pressure and weight ratio of methanol to XLPE didn't affect the reaction in experimental range. However, the effect of reaction temperature was obvious, and the complete decross-linking was achieved over 380°C. Table 1 shows the effect of solvent on the decross-linking reaction of XLPE. At 380°C, the reaction was completed in

all solvents. At 360°C, the reaction proceeded further in methanol than ethanol.

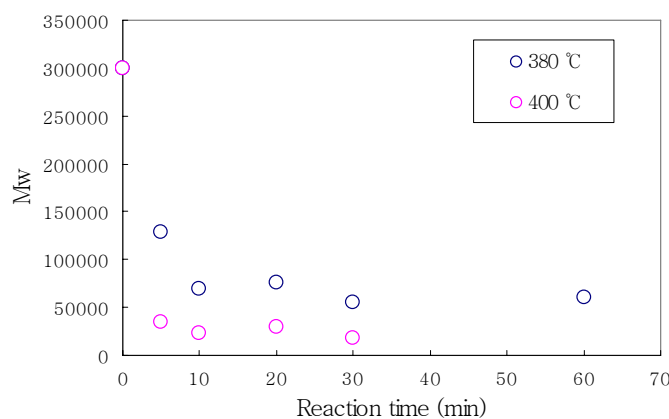


**Figure 1** : Effect of parameters on the decrosslinking reaction of XLPE in supercritical methanol (a) reaction temperature, (b) reaction pressure, (c) weight ratio of methanol to polyethylene

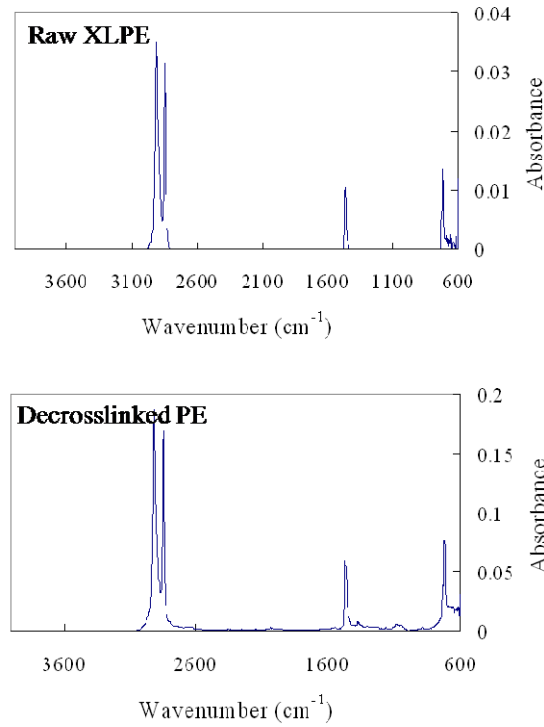
**Table 1** : Effect of solvents on the decrosslinking reaction of XLPE

Solvent	Temperature (°C)	Pressure (MPa)	Solvent/XLPE (g/g)	Reaction time (min)	Gel content (%)
Water	380	25	50	5	1.51
Methanol	360	15	20	5	21.54
Methanol	380	15	20	5	0.27
Ethanol	360	16	20	5	38.38
Ethanol	380	13	20	5	1.88
2-Propanol	380	10	20	5	1.91

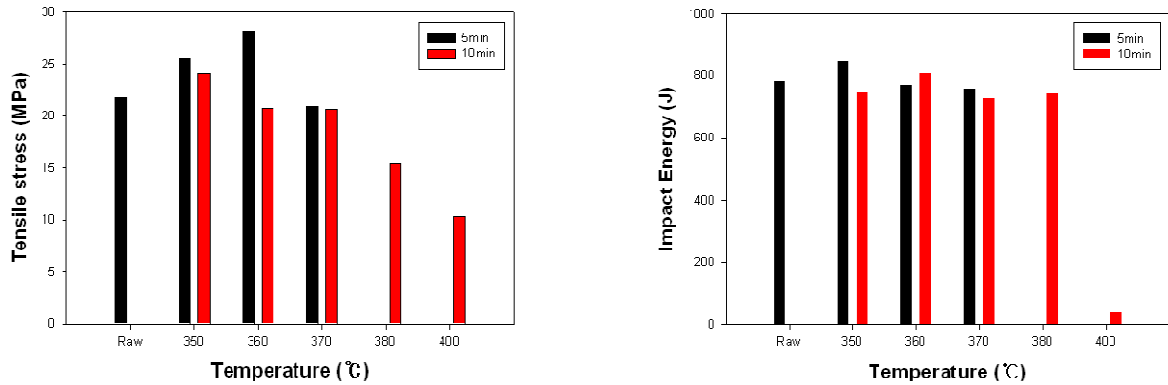
Figure 2 shows the change of molecular weight of polyethylene along with reaction temperature and reaction time [7]. The molecular weight decreased after decross-linking due to the cleavage of backbone chains. However, according the FT-IR analysis in Figure 3, no other functional groups except for methylene were formed during the reaction. As shown in Figure 4, the mechanical properties were not decreased compared with raw polyethylene. Moreover, some products with the gel content of about 10% were moldable and they showed better strength.



**Figure 2** : Change of molecular weight of polyethylene after decrosslinking reaction



**Figure 3** : FT-IR spectra of raw XLPE and decrosslinked polyethylene



**Figure 4** : Tensile strength and impact strength of raw XLPE and decrosslinked polyethylene

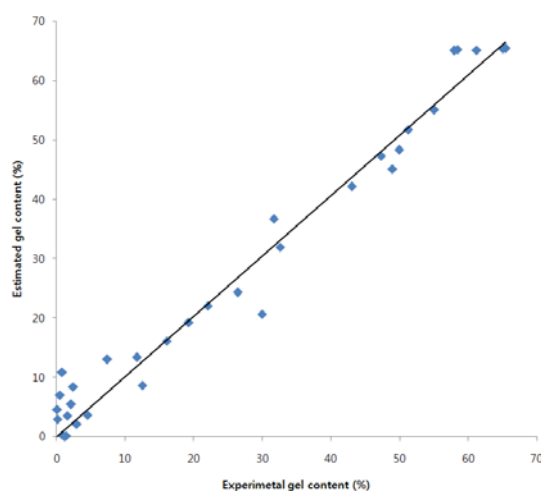
Kinetic study was carried out with the reaction model which regard reaction rate as the function of gel concentration by the 1st order [8]. The obtained rate equation was as followed.

$$\frac{dC_{gel}}{dt} = -kC_{gel,0} e^{-k(t-t_0)} \quad (1)$$

$$k = 0.0867 \pm 0.082e^{\frac{578 \pm 25}{R} \left( \frac{1}{623.15} - \frac{1}{T} \right)}$$

The estimated results by the equation (1) were fit well with the experimental results as shown

in Figure 5. Based on this, a single-screw extruder for continuous reaction was designed and operated successfully.



**Figure 5 :** Comparison of experimental and estimated gel content

## CONCLUSION

The decrosslinking reaction of XLPE in supercritical fluid was studied. Reaction temperature and solvent were dominant parameters to affect the reaction rate. Although the molecular weight of polyethylene decreased after decrosslinking reaction, no other functional groups were not formed and the mechanical strength didn't decrease. The kinetic model based on gel concentration agreed well with experimental results. The continuous decrosslinking process was possible using a single-screw extruder.

## REFERENCES :

- [1] VAN KRIEKEN, R., SERRANO, D. P., AGUADO, J., GARCIA, R., ROJO, C., *J. Anal. Appl. Pyrol.*, Vol. 58-59, **2001**, p. 127
- [2] MANOS, M., YUSOF, I. Y., GANGAS, N. H., PAPAYANNAKOS, N., *Energy & Fuels*, Vol. 16, **2002**, p. 485
- [3] MISKOLCZI, N., BARTHA, L., DEAK, G., *Polym. Degrad. Stab.*, Vol. 91, **2006**, p. 517
- [4] NEVES, I. C., BOTELHO, G., MACHDO, A. V., REBELO, P., RAMOA, S., PEREIRA, M. F. R., RAMANATHAN, A., PESCARMONA, P., *Polym. Degrad. Stabil.*, Vol. 92, **2007**, p. 1513
- [5] WATANABE, S., KOMURA, K., NAGAYA, S., MORITA, H., NAKAMOTO, T., HIRAI, S., AIDA, F., *Proceedings International Conference on Properties and Applications of Dielectric Materials*, Vol. 7, **2003**, p. 595
- [6] GOTO, T., YAMAZAKI, T., *Hitachi Cable Review*, Vol. 23, **2004**, p. 24
- [7] HONG, S. M., CHO, H., KOO, C. M., LEE, J. H., PARK, W. Y., LEE, H.-S., LEE, Y.-W., *Korean Chem. Eng. Res.*, Vol. 46, **2008**, p. 63
- [8] LEE, H.-S., JEONG, J. H., CHO, H.-K., KOO, C. M., HONG, S. M., KIM, H., LEE, Y.-W., *Polym. Degrad. Stab.*, Vol. 93, **2008**, p. 2084