

초임계유체를 이용한 가교폴리에틸렌의 탈가교화 반응의 반응속도론

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Introduction

Plastic has been used widely in the daily life for many advantages such as lightness, strength, and beautiful color. However, because it is not bio-degradable, the treatment of waste plastic has been the point at issue, so many researchers have been studied the method to reuse the waste plastic. In this study, the recycling of cross-linked polyethylene (XLPE) was focused on. The XLPE has been widely used as an insulating material for electric wires and cables because of its high insulating characteristics. However, it is very difficult to reuse it because it is a thermosetting resin, therefore, in present, most of waste XLPE have been incinerated or disposed of in landfills.

Recently, the recycling technologies for various plastic using supercritical fluid have been studied by many researchers. [1-4] Specially, Goto et al. [5] reported that the silane-cross-linked polyethylene can be de-cross-linked by supercritical alcohol, and Watanabe et al. [6] reported that the chemically-cross-linked polyethylene by supercritical water. However, these researches focused on only phenomena, didn't provide any scientific explanation. Therefore, in this paper, the effect of several parameters on the kinetics of de-cross-linking reaction of XLPE was studied.

Experimental Procedure

In this study, the radiation-cross-linked polyethylene foam having the gel content of 45, 55, 65% (provided by Youngbo Chemical Co., Ltd., Korea) was used as raw material. As supercritical fluids, water distilled by AquaMAX (Younglin Instrument Co., Ltd., Korea), methanol (99.5%, Samchun Pure Chemical Co., Ltd., Korea), ethanol (95.0%, Samcun Pure Chemical Co., Ltd.), 2-propanol (100.0%, J. T. Baker Inc., USA) were used without further purification.

The experiments were carried out in the batch reactor, which was made of stainless steel (SUS 316, Hanyang Precision Machine, Korea) as shown in Figure 1. The reaction

temperature was controlled by electric furnace with PID controller and the reaction pressure was controlled by varying the amount of solvent and XLPE. The reaction time is determined as the time from the instance that the temperature reaches target temperature until the instance that the reactor is chilled by cold water.



Figure 1. The picture of high-pressure reactor

The gel content of raw XLPE and products was measured according to the ASTM D2765. The gel content means the weight fraction of cross-linked part in polymer. After the weighed sample had been extracted in boiling xylene (Sigma-Aldrich Inc., USA) during 12 hours, the weight of residual sample was measured. The gel content is calculated using following equation.

$$\text{Gel content}(\%) = \frac{\text{Weight of residual sample after extraction (mg)}}{\text{Weight of sample before extraction (mg)}} \times 100$$

Result and Discussion

First, the feasibility of de-cross-linking was confirmed using various supercritical fluids. The results are shown in Table 1. At 380°C, the gel content fell to lower than 2% in every solvent. Especially, using supercritical alcohols, the de-cross-linking reaction was possible at relatively low pressure, that is, lower pressure than the critical pressure of water. At 360°C, the reaction rate is slower in ethanol than in methanol.

Table 1. The results of de-cross-linking experiments using various solvents.

Solvent	Temperature (°C)	Pressure (MPa)	Weigh ratio of solvent to XLPE	Reaction time (min.)	Gel content (%)
Water	380	24.5	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

In addition, the experiments were performed using the XLPE samples with various gel content. The results are shown in Table 2. As the gel content of raw XLPE is low, the gel content after reaction is low. In the case of XLPE with the gel content of 45 and 55%, the gel content decreased to very low value even at 360°C, unlike XLPE with the gel content of 65%.

Table 2. The effect of initial gel content on the reaction rate.

Initial gel content (%)	Temperature (°C)	Pressure (MPa)	Weight ratio of solvent to XLPE	Reaction time (min.)	Gel content (%)
45	340	15	20	5	21.18
45	360	17	20	5	0.43
45	380	18	20	5	0.55
55	360	16	20	5	3.56
65	360	15	20	5	21.54

The Figure 2 shows the rate of de-cross-linking reaction at different temperatures. At 320°C, the gel content was not changed until 20 minutes. However, at 360°C, the gel content decreased dramatically in very short time (30 seconds) and decreased slowly along the reaction time. From these results, it is supposed that the rate of de-cross-linking reaction of XLPE is determined by the reaction temperature dominantly.

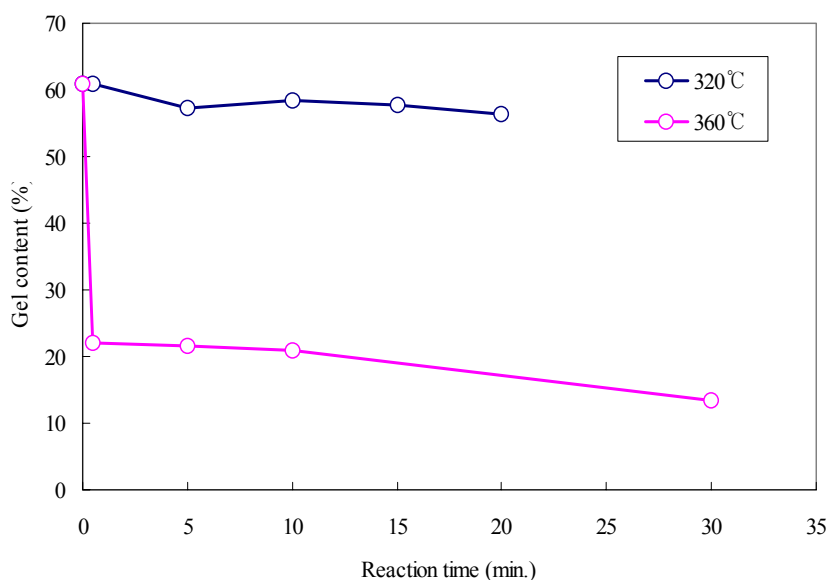


Figure 2. The rate of de-cross-linking reaction at different temperatures

Conclusion

In this study, the rate of de-cross-linking reaction of XLPE in supercritical fluids was investigated. The XLPE was able to be completely de-cross-linked using various supercritical fluids other than water. In addition, it was possible to de-cross-link the XLPE with low gel content at relatively low temperature. In conclusion, it is supposed that the dominant factor to determine the rate of de-cross-linking reaction is the reaction temperature. From the results of this study, the important information about the reaction kinetics of de-cross-linking of XLPE in supercritical fluids can be obtained.

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