

# Selective Decomposition of the Siloxane Bond Constituting the Crosslinking Element of Silane-Crosslinked Polyethylene by Supercritical Alcohol

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**ABSTRACT:** Material recycling of silane-crosslinked polyethylene (silane-XLPE) was investigated to make thermoplastic polyethylene (PE). To make thermoplastic PE from silane-XLPE, a crosslinking element that consists of a siloxane bond must selectively be decomposed. Supercritical alcohol and water were adopted in this study. An autoclave was applied to expose silane-XLPE to the supercritical fluid. The structure of the products was analyzed with <sup>29</sup>Si-NMR, Fourier transform infrared, gel fraction, and molecular weight measurements. The results showed that the siloxane bond was successfully decomposed selectively by supercritical alcohol. It was expected that the structure of the recycled PE would be close to that of the silane-grafted PE. To confirm this expectation, the recycled PE was cured in saturated water vapor to investigate the crosslinking ability. The recycled

PE, silane-grafted PE, and silane-grafted PE with a catalyst for condensation were compared. The kinetics and activation energy were calculated from the data of the temperature dependence of the increment of the gel fraction. The results showed that the recycled PE still had the ability to undergo a crosslinking reaction. The kinetics and activation energy of the recycled PE were closer to those of silane-grafted PE than to those of silane-grafted PE with a catalyst. The activity of the catalyst must have been lost by supercritical alcohol. These data support the expectation of the structure of the recycled PE. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 144–151, 2008

**Key words:** crosslinking; polyethylene (PE); processing; reactive extrusion; recycling

## INTRODUCTION

Crosslinked polyethylene (XLPE) is widely used as an insulator of wires and cables. XLPE is renowned as a material difficult to recycle because of its low fluidity and bad moldability caused by crosslinking. Therefore, most industrial XLPE waste is burned as a fuel or buried.<sup>1</sup>

In a previous study,<sup>2</sup> XLPE waste was mixed with polyethylene (PE) in an extruder to make a thermoplastic recycled polymer. However, a random decomposition of the polymer chain of XLPE occurred. As a result, the mechanical properties of the products could not be kept the same as those from the use of only virgin PE. Other reports have shown that powdered XLPE can be used as a filler of the polymer.<sup>3,4</sup> However, these studies require further investigation of the applications of the recycled

product and the development of a market and so forth because of the apparent difficulty in directly using the recycled product as insulation for wire or cables (closed recycling).

We herein report a technique for closed recycling of silane-crosslinked polyethylene (silane-XLPE). The fluidity and bad moldability of silane-XLPE should be improved for closed recycling without deterioration of the properties. The origin of the low fluidity and bad moldability is the crosslinking element. Therefore, selective decomposition of the crosslinking element is the ideal process for closed recycling.

The crosslinking element of silane-XLPE consists of a siloxane bond, which can be decomposed by alcohol or water. However, these molecules cannot reach the siloxane bond in silane-XLPE at room temperature and pressure because alcohol or water cannot dissolve into XLPE, each having a different polarity.

On the contrary, the polarity of supercritical alcohol and water can be controlled over a wide range.<sup>5,6</sup> For this reason, supercritical fluid was applied to the recycling of silane-XLPE, which is a hydrophobic polymer.<sup>7–9</sup>

The general problem of treating polymer waste by a supercritical fluid is the chemical process for com-

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mercialization. To solve this problem, we propose a continuous process for the treatment of XLPE by supercritical methanol.<sup>10-12</sup> This means that the process for the industrialization of this technique will appear. Furthermore, the reaction conditions for the recycling and the reactivity of the products should be studied to put this technique to practical use.

In this article, we primarily describe the reaction conditions in supercritical water and alcohol. Then, the structure of the product and the chemical reaction in the supercritical alcohol are also examined. Furthermore, the possibility of closed recycling is discussed through an evaluation of the crosslinking ability of the recycled PE.

EXPERIMENTAL

Materials

Low-density PE from UBE Industry, Ltd. (Tokyo, Japan), was used as raw PE; the density and melt flow rate were 0.920 g/cm<sup>3</sup> and 1.0 g/10 min, respectively.

Vinyl trimethoxysilane and dibutyltin dilaurate, produced by Chisso Co. (Tokyo, Japan) and Sakai Chemical Industry Co. (Sakai-Si, Japan), respectively, were applied. Dicumyl peroxide, supplied by Mitsui Chemicals (Tokyo, Japan), was used as peroxide for grafting the vinyl silane. The purity of the methanol, made by Wako Chemicals Co. (Odawara-Si, Japan), was 99%.

Sample preparation

Raw PE was mixed with peroxide, vinyl trimethoxysilane, and dibutyltin dilaurate by a single-screw extruder at 200°C. The diameter and length/diameter ratio of the extruder were 100 mm and 30, respectively. The peroxide and vinyl trimethoxysilane were added for grafting the alkoxysilane to PE before reactive extrusion. Then, dibutyltin dilaurate, used as a catalyst for the condensation of alkoxysilane, was injected into the extruder after the melting process. As a result of the mixing of these materials, the silane-grafted PE was extruded. The silane-XLPE was obtained after the silane-grafted PE was exposed to saturated water vapor at 80°C for 24 h. Three types of additive compositions were prepared, as shown in Table I. The sample (1) series was prepared as silane-XLPE (the same as the insulation of cable and wire). The sample (2) series was prepared for spectrum analysis to reveal the structure. The sample (3) series was used to investigate the capacity for condensation.

Decomposition by the supercritical fluid

Methanol was used as supercritical alcohol. The critical points of each material are shown in Table II. Silane-XLPE was also decomposed by subcritical-to-

TABLE I  
Sample Identification of Each Step To Make Silane-XLPE

	Sample								
	(1)-1	(1)-2	(1)-3	(2)-1	(2)-2	(2)-3	(3)-1	(3)-2	(3)-3
Vinyl trimethoxysilane (wt %)	8.9 × 10 <sup>-1</sup>	8.9 × 10 <sup>-1</sup>	8.9 × 10 <sup>-1</sup>	4.7	4.7	4.7	8.9 × 10 <sup>-1</sup>	8.9 × 10 <sup>-1</sup>	8.9 × 10 <sup>-1</sup>
Dicumyl peroxide (wt %)	4.9 × 10 <sup>-2</sup>	4.9 × 10 <sup>-2</sup>	4.9 × 10 <sup>-2</sup>	2.4 × 10 <sup>-1</sup>	2.4 × 10 <sup>-1</sup>	2.4 × 10 <sup>-1</sup>	4.9 × 10 <sup>-2</sup>	4.9 × 10 <sup>-2</sup>	4.9 × 10 <sup>-2</sup>
Dibutyltin dilaurate (wt %)	4.9 × 10 <sup>-2</sup>	4.9 × 10 <sup>-2</sup>	4.9 × 10 <sup>-2</sup>	9.5 × 10 <sup>-2</sup>	9.5 × 10 <sup>-2</sup>	9.5 × 10 <sup>-2</sup>	0	0	0
Crosslinking	None	Done	Done	None	Done	Done	None	Done	Done
Recycling	None	None	Done	None	None	Done	None	None	Done
Notation	Silane-grafted PE	Silane-XLPE	Recycled PE	Silane-grafted PE	Silane-XLPE	Recycled PE	Silane-grafted PE	Silane-XLPE	Recycled PE

**TABLE II**  
Critical Points of Water and Methanol

	Methanol	Water
Temperature (°C)	239.6	374.3
Pressure (MPa)	8.0	21.8

supercritical water. The gel fraction of silane-XLPE used here was 60 wt %. The sample form was an approximately 3-mm pellet. At first, 0.5 g of silane-XLPE and 5.0 g of methanol or 10.0 g of water were enclosed in an autoclave made from austenitic stainless steel made from 18% of chrome, 12% nickel and 18% of molybdenum (SUS316). The diameter and depth inside the autoclave were 16 and 100 mm, respectively. A manometer was attached through the intermediary of a pipe made of SUS316 to measure the pressure in the autoclave. Then, the autoclave was heated by a salt bath, which had been heated at an arbitrary temperature after the air in the autoclave had been substituted by argon gas to prevent the oxidation of silane-XLPE. An arbitrary temperature for the reaction was kept for 30 min, then the autoclave was chilled with water at room temperature, and the products were taken out from the autoclave.

#### Analysis of the structure

The gel fraction for characterizing the crosslinking density was determined as follows. The weight of each specimen ( $W_f$ ) was measured before it was immersed in xylene at 110°C. The rest of the abstraction was taken out from the xylene and dried at 80°C under vacuum aspiration for more than 4 h. The weight of the dried specimen ( $W_a$ ) was also measured. The gel fraction was calculated from the weight of the specimen before and after abstraction with the following equation:

$$\text{Gel fraction (wt \%)} = (W_a/W_f) \times 100$$

The molecular weight, which was the index of decomposition of the PE main chain, was measured by high-temperature gel permeation chromatography [HLC-8121GPC/HT, Tosoh (Tokyo, Japan); column: TSKgel GMHr-H(S)HT]. A 0.05% solution of each specimen was made. The specimens were dissolved in *o*-dichlorobenzene with 0.1% 2,6-di-*t*-butyl-4-methyl phenol at 130°C. A master curve for the determination of the molecular weight was made from standard polystyrene.

The chemical structure of the crosslinking element of the products derived from supercritical methanol was analyzed with  $^{29}\text{Si}$ -NMR and Fourier transform infrared (FTIR) spectrometry.

The FTIR spectra were obtained by transmittance with a Jasco MFT2000 (Tokyo, Japan). A 0.5-mm

sheet of each specimen for FTIR was prepared through pressing at 180°C.

The NMR experiment was carried out on a Bruker ASX400 spectrometer (Osaka-Si, Japan) with transmitter frequencies of 400.13 MHz for  $^1\text{H}$  and 79.49 MHz for  $^{29}\text{Si}$ -NMR. The high-resolution solid-state  $^{29}\text{Si}$ -NMR spectra were obtained by the combined use of high-power  $^1\text{H}$  dipolar decoupling and magic angle spinning.  $^{29}\text{Si}$  chemical shifts were expressed with respect to tetramethylsilane (0 ppm). The measurement range was 25 kHz.

#### Condensation ability of recycled PE

Specimens (1)-1, (1)-3, and (3)-1 were cured in saturated water vapor at 40, 60, and 80°C. After the specimens were extracted from the saturated water vapor, the gel fraction was determined to evaluate the ability to crosslink.

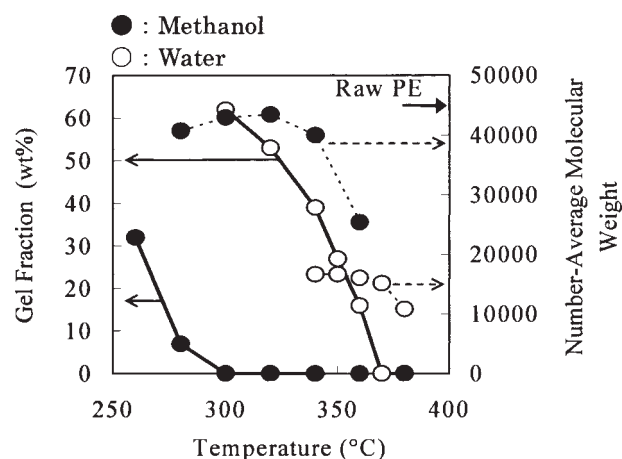
## RESULTS AND DISCUSSION

#### Analysis of the chemical reaction in the supercritical fluid

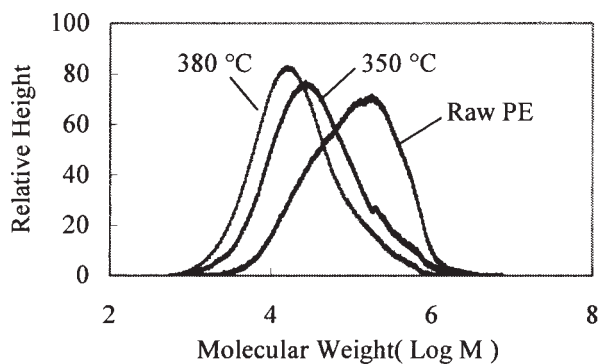
The gel fraction and molecular weight of the products versus the decomposition temperature are shown in Figure 1. The gel fraction vanished over 300°C when methanol was used as the supercritical fluid. With water, a temperature over 370°C was necessary to reduce the gel components to 0 wt %.

The molecular weight decreased over 340°C with water and methanol. This result agrees with the general knowledge of the thermal decomposition temperature of PE.

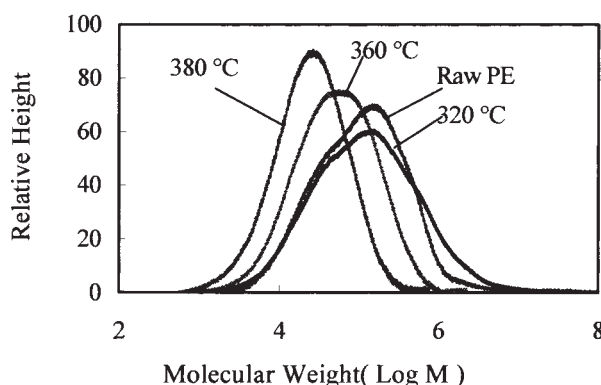
By the use of water, the molecular weight of the products was lower than that of raw PE whenever the gel fraction of the products decreased to 0%. This indicated that the reaction in supercritical water



**Figure 1** Gel fraction and molecular weight of recycled PE made with supercritical fluid.



(a) by supercritical water



(b) by supercritical methanol

**Figure 2** Molecular weight distribution of recycled PE made with supercritical fluid.

was selective not only for the crosslinking element but also for the main chain of PE.

On the other hand, when methanol was applied, the molecular weight was kept equal to that of raw PE when the gel fraction diminished at 300–340°C.

The molecular distribution of the products is shown in Figure 2. The product made with water obviously had a lower molecular weight than raw PE. However, the products made at 320°C with methanol had a molecular weight distribution similar to that of raw PE. These results are positive evidence for the selective reaction of crosslinking elements by supercritical alcohol.

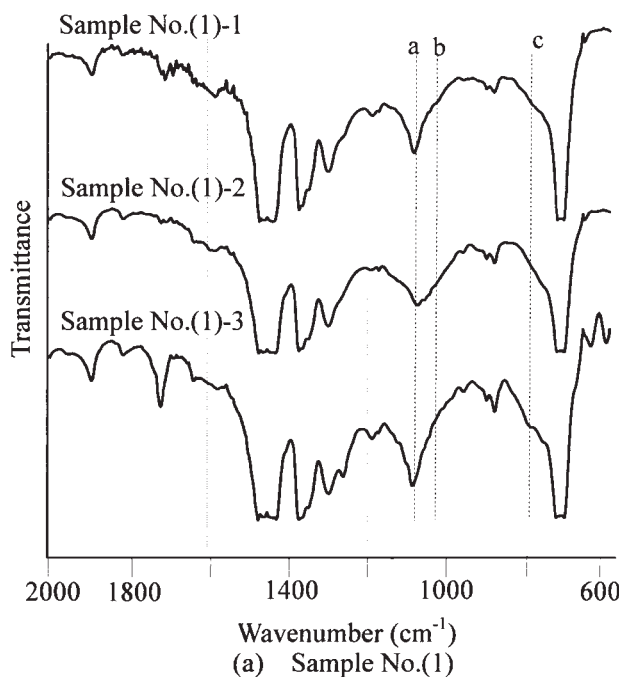
The assignment of the peak in the IR spectra of silane-grafted PE, silane-XLPE, and recycled PE is shown in Table III. In previous studies,<sup>13,14</sup> it was

**TABLE III**  
IR Absorption Frequencies Related to the Silane-Crosslinking Unit<sup>10,11</sup>

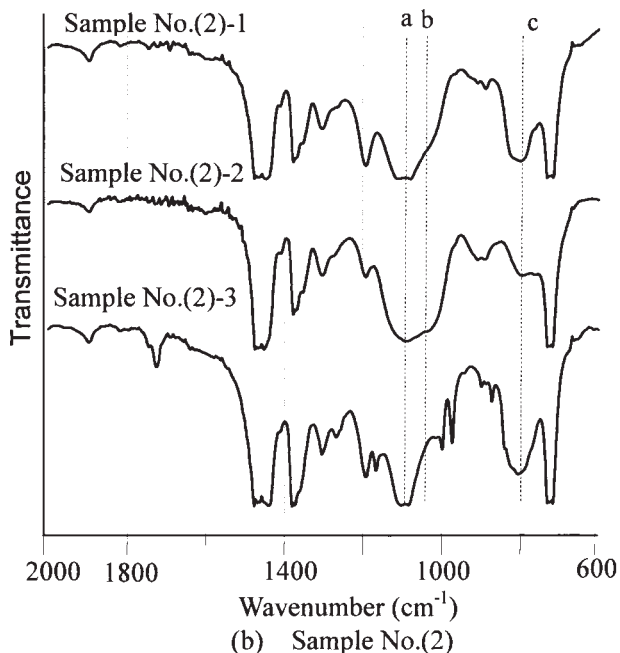
Wave number (cm <sup>-1</sup> )	Structure
800	—SiOCH <sub>3</sub> or —SiOH
1030	—Si—O—Si—
1090	—SiOCH <sub>3</sub> or —SiOH

revealed that peak b at 1030 cm<sup>-1</sup> represented the siloxane bond and peaks a and c were related to the alkoxy silane or hydroxysilane.

The spectra of the sample (1) and (2) series are shown in Figure 3(a,b), respectively. The difference between the series of the spectra of sample (1) was small, but the shoulder of peaks b and c could be observed. The concentration of the siloxane bond was too small to compare the chemical structures of the samples by FTIR.



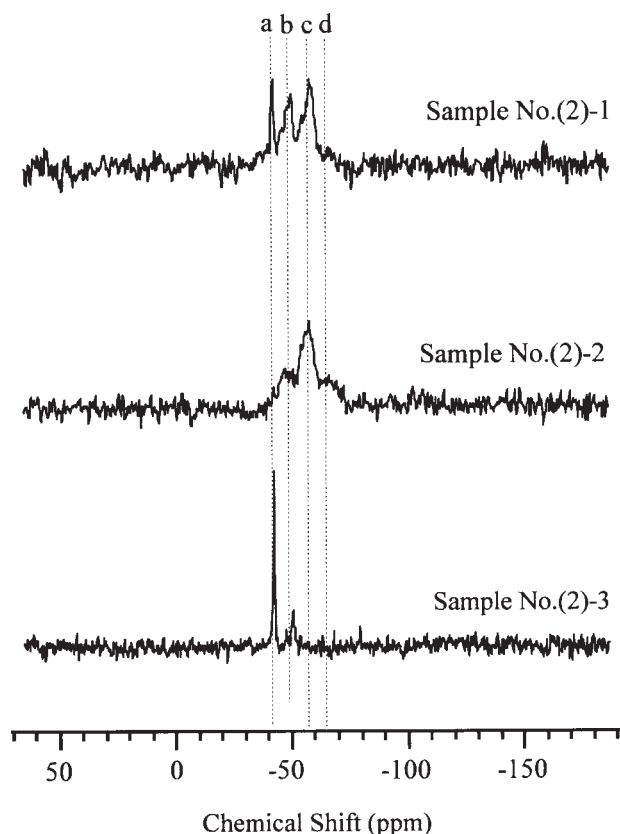
(a) Sample No.(1)



(b) Sample No.(2)

**Figure 3** IR spectra of silane-grafted PE [samples (1)-1 and (2)-1], silane-XLPE [samples (1)-2 and (2)-2], and recycled PE [samples (1)-3 and (2)-3].





**Figure 4**  $^{29}\text{Si}$ -NMR spectra of silane-grafted PE [sample (2)-1], silane-XLPE [sample (2)-2], and recycled PE [sample (2)-3].

On the other hand, there was a difference between the series of the spectra of sample (2), which had a concentration of the siloxane bond 5.3 times greater than that of sample (1). Peak b was clearly observed as the shoulder of peak a in the spectrum of sample (2)-2. Peak c was observed in samples (2)-1 and (2)-3. On the contrary, peak c was small in sample (2)-2. These results indicated that the structure of sample (2)-3 was close to that of silane-grafted PE.

$^{29}\text{Si}$ -NMR spectra are shown in Figure 4. The four peaks related to the Si—O bond were observed. The broad peak was observed at peaks b (−49 ppm), c (−57 ppm), and d (−65 ppm). A sharp peak was observed at peak a (−41 ppm) in the spectra of sample (2)-3.

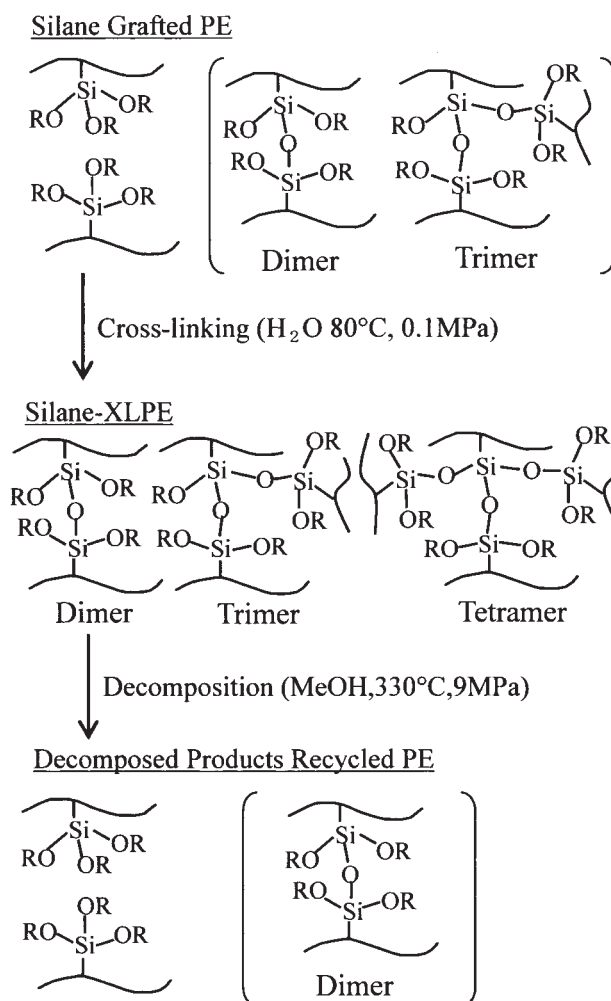
**TABLE IV**  
 $^{29}\text{Si}$ -NMR Chemical Shifts of Silane-XLPE

Peak	Chemical shift (ppm)	Number of —O—Si bonds coupled on the Si atom	Structure
a	−41	0	$\equiv\text{Si—OH}$ or $\equiv\text{SiOCH}_3$
b	−49	1	$\equiv\text{Si—O—Si}\equiv$
c	−57	2	$=\text{Si}(\text{—O—Si}\equiv)_2$
d	−65	3	$-\text{Si}(\text{—O—Si}\equiv)_3$

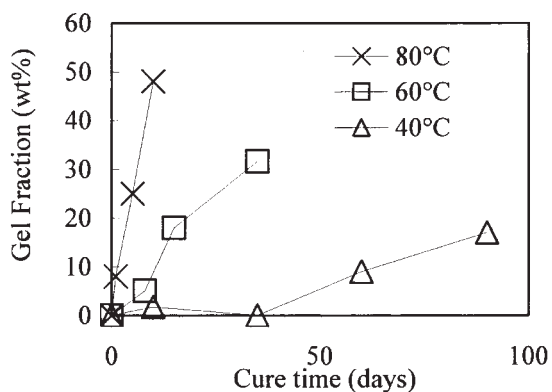
In a previous study,<sup>15</sup> it was revealed that the  $^{29}\text{Si}$ -NMR spectrum of ethyltrimethoxysilane has a peak around −40 ppm related to the alkoxide group (OR) or hydroxyl group (OH). Generally, these peaks shift to lower frequencies in the condensation process of a silicate solution forming a siloxane bond.<sup>16</sup> The peaks related to the siloxane bond must be broader than that of the alkoxide group because the molecular movement of  $^{29}\text{Si}$  is restricted. On the basis of this study, each peak was assigned to the structure shown in Table IV.

By the use of this assignment, the  $^{29}\text{Si}$ -NMR spectrum of the series of sample (2) can be understood as follows. There were peaks a, b, c, and d in the spectrum of (2)-1. In the spectrum of (2)-2, peak a disappeared. After silane-XLPE was exposed to supercritical methanol, peaks c and d vanished, and peak b became small; then, sharp peak a appeared.

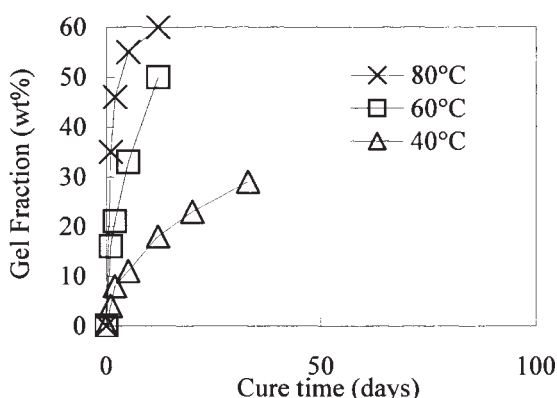
These results revealed the structure shown in Figure 5. There were three types of crosslinking elements in silane-XLPE. It was indicated that silane-



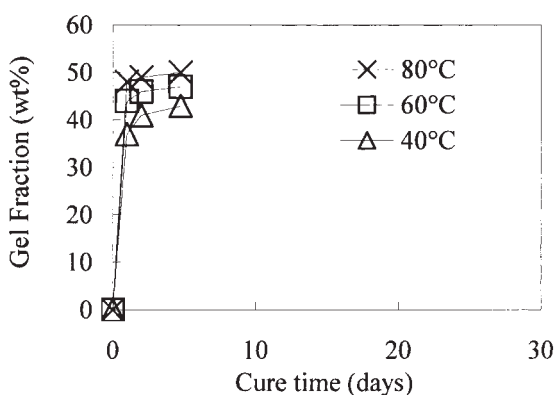
**Figure 5** Structures of silane-grafted PE [sample (2)-1], silane-XLPE [sample (2)-2], and recycled PE [sample (2)-3].



(a) Sample No.(1)-3



(b) Sample No.(3)-1



(c) Sample No.(1)-1

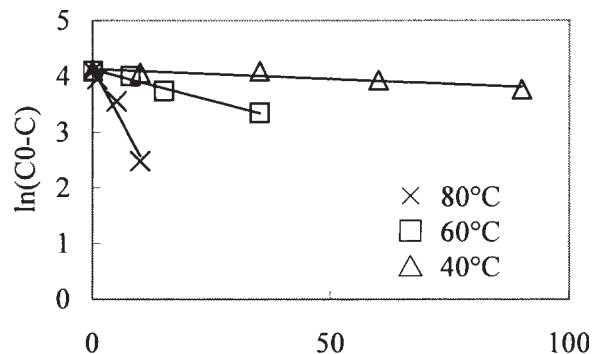
**Figure 6** Variation of the gel fraction of recycled PE [sample (1)-3], silane-grafted PE without a catalyst [sample (3)-1], and silane-grafted PE with a catalyst [sample (1)-1] in saturated water vapor.

grafted PE was partially crosslinked. In silane-XLPE, alkoxysilane could not be observed, but siloxane bonds as dimer and trimer were observed. After XLPE was exposed to the supercritical alcohol, the siloxane bond was decomposed to the alkoxysilane, but a small amount of the dimer still remained.

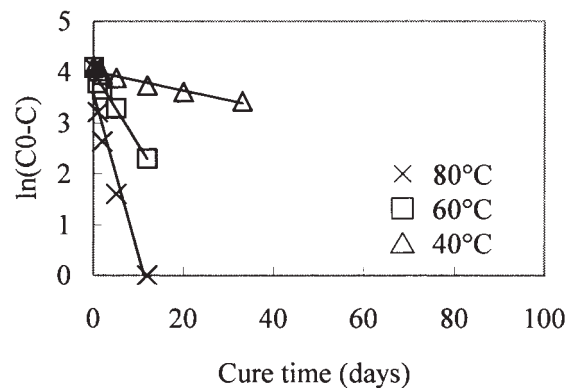
These results indicated that the siloxane bond was decomposed to the alkoxysilane in supercritical alcohol, and this well agreed with the analysis by FTIR.

The structure appearing here suggests that the structure of recycled PE is close to that of silane-grafted PE. It is expected that recycled PE can be crosslinked by the condensation of the alkoxide group (OR) or hydroxyl group (OH).

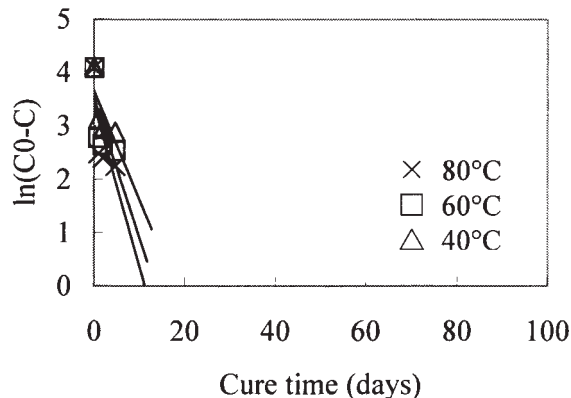
Therefore, recycled PE must have the ability to crosslink if these structures revealed here are correct.



(a) Sample No.(1)-3



(b) Sample No.(3)-1



(c) Sample No.(1)-1

**Figure 7** Rate constant of recycled PE [sample (1)-3], silane-grafted PE without a catalyst [sample (3)-1], and silane-grafted PE with a catalyst [sample (1)-1]. The solid line was calculated by the least-squares method.

**TABLE V**  
Calculated Values of Rate Constant  $k$

		$k$ (day <sup>-1</sup> )		
		(1)-3	(3)-1	(1)-1
Temperature (°C)	40	$3.6 \times 10^{-3}$	$4.0 \times 10^{-2}$	$2.0 \times 10^{-1}$
	60	$2.2 \times 10^{-2}$	$1.4 \times 10^{-1}$	$2.6 \times 10^{-1}$
	80	$1.6 \times 10^{-1}$	$3.2 \times 10^{-1}$	$3.0 \times 10^{-1}$

### Condensation ability of recycled PE

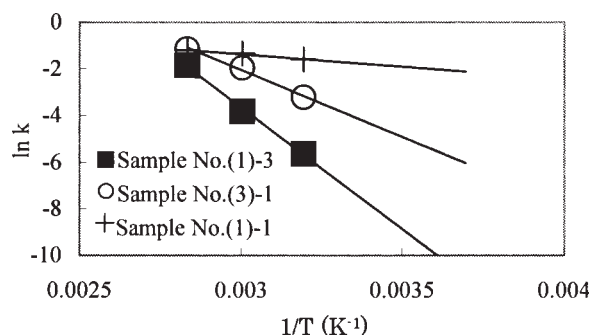
The product was cured in saturated water vapor to evaluate the ability to crosslink by condensation. The variation of the gel fraction of recycled PE is shown by a comparison of sample (1)-3 with sample (3)-1 and sample (1)-1 in Figure 6.

The gel fraction of sample (1)-3 increased with time. These results show that recycled PE can be crosslinked, and this supports the results of the analysis of the chemical structure of recycled PE. The increased rate of the gel fraction of the recycled PE was lower than that of silane-grafted PE with a catalyst. At 40°C, a 0 wt % gel fraction was kept over 30 days, which could be long enough to practically use recycled PE as PE.

To evaluate the reactivity, we calculated the rate constant of crosslinking ( $k$ ), which was represented by the gel fraction. A pseudo-first order was applied here. The rate equation of the pseudo-first order is represented as follows:

$$\ln(C_0 - C) = -kt + A$$

where  $C_0$  represents the ideal gel fraction after the condensation reaction is completed (it was assumed to be 0.6 g/g here, i.e., the same as that of XLPE before saturation by supercritical methanol),  $C$  represents the gel fraction at an arbitrarily set moment,  $A$  is a constant, and  $t$  is the time during which the specimens are saturated in water vapor for condensation.



**Figure 8** Arrhenius plot of rate constant  $k$  for the crosslinking reaction of silane-XLPE.

**TABLE VI**  
Calculated Values of  $E'_a$

Sample	$E'_a$ (J/mol)
(1)-3	$8.7 \times 10^4$
(3)-1	$4.8 \times 10^4$
(1)-1	$9.0 \times 10^3$

$\ln(C_0 - C)$  versus  $t$  is plotted in Figure 7. The solid lines were obtained by the least-squares method. The solid line well fitted the measured variation of the gel fraction. The calculated rate constant ( $k$ ) is presented in Table V. The parameter  $E'_a$ , with respect to the activation energy, was determined as follows.

$$\ln k = \ln A' - E'_a/RT$$

where  $T$  is the temperature,  $R$  is the gas constant, and  $A'$  is the characteristic constant of the reaction. In Figure 8,  $\ln k$  is plotted against  $1/T$  to obtain the activation energy (shown by the solid line).  $E'_a$  was calculated by the least-squares method. The calculated  $E'_a$  values are shown in Table VI. The order of the activation energy for the condensation of recycled PE was closer to that for the silane-grafted PE without a catalyst than to that for the silane-grafted PE with a catalyst. This indicated that the catalyst in the recycled PE had been inactivated.

### CONCLUSIONS

Silane-XLPE turned into thermoplastic PE after it was heated in supercritical methanol as a result of the selective decomposition of the siloxane bond by supercritical methanol. The chemical structure of the recycled PE was close to that of silane-grafted PE.

Moreover, we investigated the condensation of the recycled PE. The kinetics of the condensation of the recycled PE was slower than that of silane-grafted PE, and this meant that the catalysis had been inactivated in the recycled PE. For fast condensation, dibutyltin dilaurate was as effective a catalyst for the condensation of the recycled PE as for the condensation of silane-grafted PE. These data give us an idea about the recycling of silane-XLPE as silane-XLPE.

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