

An Investigation of Water Crosslinking Reactions of Silane-Grafted LDPE

YEONG-TARNG SHIEH, JIA-SHENG LIAU, TZUNG-KAI CHEN

Department of Chemical Engineering, National Yunlin University of Science and Technology, Touliu, Yunlin 640, Taiwan, Republic of China

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ABSTRACT: Factors—including time, temperature, morphology, and thickness of sample, the extent of silane grafting, and water concentration—that affect the rate and degree of water crosslinking reactions of the silane-grafted LDPE are investigated. The gel content of the water-crosslinked sample increases with increasing time, temperature, and water concentration, but with decreasing content of the crystalline component in the sample and thickness of the sample. The relationship between the gel content and the crosslinking time is dependent on thickness and morphology of the sample, and the extent of silane grafting in the sample. The crosslinking rates and the resultant gel content are inversely proportional to the content of crystalline component of the sample, suggesting that the crosslinking reactions occur mainly in the amorphous domain of the sample. For those samples with high resultant gel contents, the crystallizations of the samples are significantly enhanced by crosslinking when the gel contents are higher than about 40%, leading to a dual relationship between the gel contents of the samples and the crosslinking times. For low temperatures, the rate-determining step of the crosslinking reactions is the diffusion of water, rather than the hydrolysis and the subsequent condensation reactions of the silyl trimethoxy groups. For high temperatures and high extents of silane grafting in the samples, however, the chemical reactions dominate the crosslinking process. The overall activation energy of the crosslinking reactions is dependent on thickness of the sample. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 186–196, 2001

Key words: polyethylene; silane grafting reactions; crosslinking reactions; gel content; diffusion of water

INTRODUCTION

Polyethylene has long been known as an excellent dielectric for use as an insulation material in power cable constructions. It has the advantages of excellent electrical properties, excellent resistance to cold flow, ease of processing, adequate mechanical properties and, notably, excellent

value (cost and performance). The major drawback of thermoplastic polyethylene is its relatively low upper use temperature. By crosslinking the material, this temperature limitation is overcome, and the upper use temperature is increased.

There are a variety of ways to achieve the crosslinking of polyethylene.¹ Polyethylene has no functional groups, which can provide crosslinking capability, such as the kind one finds in typical thermosetting resins. The most common way is through the use of peroxide crosslinking agents added to the resin. The peroxides provide a source of free radicals when heated above their decomposition temperatures. These free radicals

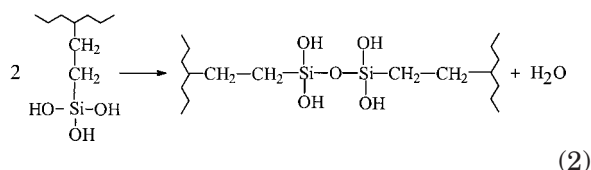
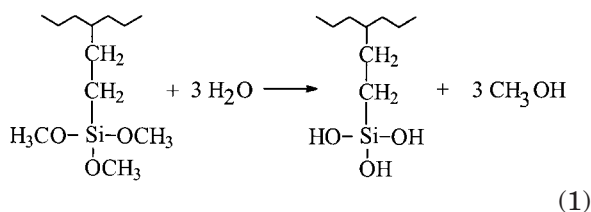
Correspondence to: Y.-T. Shieh.

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are capable of extracting hydrogens from the polyethylene backbone thus transferring the free radical site to the polyethylene. With this accomplished, two polyethylene chains can be crosslinked. A second method of crosslinking polyethylene is through the use of irradiation. In this case, the free radical formed on the polyethylene backbone is the result of electron beam irradiation. The third type of crosslinking is through the grafting of a silane onto the polyethylene and subsequently through the condensation reaction of the silane graft by moisture.

The way of making crosslinkable polyethylene through the silane grafting has gained much attention in recent years because of its various advantages, such as easy processing, low cost and capital investment, and favorable properties in the processed materials. The most common silane used in the manufacture of silane crosslinkable polyethylene is vinyl trimethoxysilane. This silane has conventionally been introduced into polyethylene by melt grafting using a peroxide. In producing the crosslinkable silane-grafted polyethylene, a peroxide is mixed with the silane and polyethylene and all these components are compounded in an extruder at high temperature. The silane-grafted polyethylene is then crosslinked by water. Hjertberg and coworkers² studied the crosslinking reactions of an ethylene vinyl trimethoxysilane copolymer that was treated in water at 90°C. The kinetics of the crosslinking was followed by measuring the gel content and by determination of the content of different groups ($-\text{Si}-\text{OCH}_3$, $-\text{Si}-\text{OH}$, and $-\text{Si}-\text{O}-\text{Si}-$) using FTIR. The crosslinking reactions of the silane-grafted polyethylene were demonstrated to be through hydrolysis of the silyl trimethoxy groups with water followed by condensation of the formed silanol groups as follows:



Hjertberg and coworkers² did not study the effects of temperature and thickness of the sam-

ple on the reactions. Sen and colleagues³ studied the moisture crosslinking of the silane-grafted polyethylene in the presence of a catalyst. The effects of the structures of three catalysts (stannous octoate, dibutyl tin dilaurate, and dialkyl tin mercaptide), their concentrations, moisture concentration, temperature, and time on degree and rate of crosslinking were evaluated. Crosslinking reactions were found to be first order with respect to both catalyst and moisture. Sen and coworkers, however, did not study the effects of temperatures and thickness of the sample on the reactions in the absence of catalyst. Bullen and coworkers⁴ studied the crosslinkings of the ethylene-vinyl trimethoxysilane copolymers during high temperature melt processing using melt rheological and infrared spectroscopic techniques. Two environmental factors including oxidation of the polymer and the presence of catalyst (dibutyl tin dilaurate) were shown to be major contributors to the crosslinking formation. The catalyst under anhydrous conditions at processing temperatures could initiate the crosslinking, but the mechanism of crosslinking was not elucidated. Narkis and coworkers⁵ studied the crosslinking progress in different environments at various temperatures. Some properties including mechanical properties of the silane-grafted moisture-crosslinked polyethylene were followed as a function of crosslinking conditions. In our previous articles, we have studied kinetics of silane grafting reactions of LDPE, LLDPE, and HDPE^{6,7} and thermal properties of the silane-grafted water-crosslinked LDPE⁸ in addition to other reports.⁹⁻¹¹ The aim of this work is to study the water crosslinking reactions of the silane-grafted LDPE. Factors that affect the rate and degree of crosslinking of the polymer were investigated. These factors include time, temperature, morphology and thickness of sample, the extent of silane grafting, and the diffusion of water.

EXPERIMENTAL

Materials

All materials were used as received. LDPE (H0100) was received from Asia Polymer Corporation (Taipei, Taiwan) with a melt index (ASTM D1238) of 0.5 and a density (ASTM D1505) of 0.922 g/cm³. Dicumyl peroxide, used as an initiator for silane grafting reactions of LDPE, was supplied by Aldrich Chemical Company (Milwaukee, WI). The silane used was vinyl trimethoxysi-

lane and was received from Tokyo Kasei Kogyo Co (Tokyo, Japan).

Sample Preparations

Silane-grafted LDPE was prepared by melt extrusion of LDPE with 0.05 phr (part of reagent per hundred parts of LDPE) of dicumyl peroxide and various amounts (including 1, 3, and 5 phr) of vinyl trimethoxysilane. The extruder was operated at a speed of 20 rpm and at temperatures ranging from 170°C at the feeding zone to 190°C at the metering zone to 210°C at the die zone of the extruder (single screw of 50 mm in diameter, L/D 19, compression ratio 3.5). The resultant silane-grafted LDPE pellets from the extrusion were then loaded in between two stainless steel sheets and were compressed at 140°C for 2 min to make film samples. A spacer located in between the two stainless steel sheets controlled the thickness of the film sample. The film samples with resultant thicknesses of 0.53 and 1.02 mm were then immersed into water at a constant temperature (including 60, 70, 80, 90, and 100°C) for a certain of time to conduct crosslinking reactions. For comparison purpose, the sample of 0.53 mm in thickness was hung in an oven at 80°C with constant relative humidity at 35 and 77% for the same period of time as above to conduct crosslinking reactions.

Analyses

Degrees of crosslinking of the silane-grafted water-crosslinked samples were measured by determining their gel contents after crosslinking reactions. The determination of the gel content was performed by extracting the soluble component from the sample using decalin with refluxing at 190°C for 6 h. Fourier transform infrared (FTIR, Bio-Rad FTS155) spectroscopy was used for characterization of silane grafting reactions of LDPE. Differential scanning calorimeter (DSC, TA Instruments, DSC 2010) was used for characterization of endothermic melting behavior of LDPE, silane-grafted LDPE, and silane-grafted water-crosslinked LDPE for the purpose of correlating the crosslinking reactions and morphologies of samples. DSC analysis was performed at a heating rate of 10°C/min from 30 to 150°C, followed by cooling at the same rate to 30°C and then heating again at the same rate to 150°C to obtain the second endotherms. The integration of the endothermic peak area was performed by using the software supplied by TA Instruments, Co. The

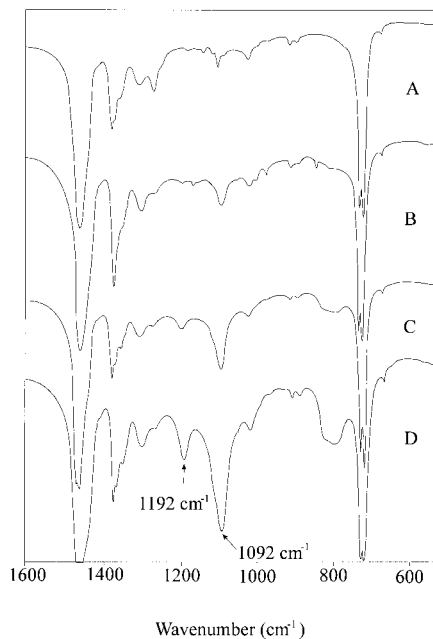


Figure 1 FTIR spectra of LDPE samples that have reacted with (A) 0 phr, (B) 1 phr, (C) 3 phr, and (D) 5 phr of silane.

type of baseline for connecting the start and the end of the endothermic peak was the sigmoidal line with horizontals at the start and the end of the peak. Polarized optical microscope (POM, Zeiss D-07740) was used for characterization of crystal morphologies of samples. Samples for POM characterization were prepared by casting from xylene followed by heating in a hot stage under nitrogen to 180°C holding for 5 min and then cooling at a rate of 10°C/min to 85°C holding for 10 min. The heat-treated samples were then transferred to POM to characterize their crystal morphologies.

RESULTS

Figure 1 shows FTIR spectra of LDPE before (spectrum A) and after grafting with 1, 3, and 5 phr of silane (spectra B, C, and D, respectively). Because the peaks at 1092 and 1192 cm^{-1} are assigned to the functional group $\text{Si}-\text{OCH}_3$,^{2,3,12,13} the silane grafting reactions thus have occurred as can be seen from spectra B–D. The order of the grafting extent is consistent with that of the amount of silane used; that is, the grafting extent for the sample grafting with 5 phr silane is the highest and the sample grafting with 1 phr silane is the least.

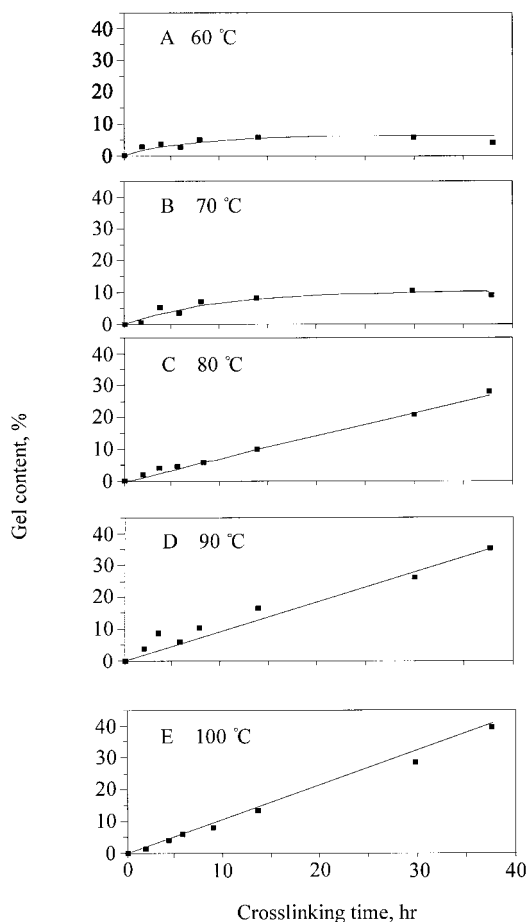


Figure 2 Plots of the gel contents of the 1-phr silane-grafted LDPE film samples with 0.53 mm in thickness as a function of crosslinking time at (A) 60°C, (B) 70°C, (C) 80°C, (D) 90°C, and (E) 100°C.

Figures 2 and 3 show plots of gel content of the silane-grafted water-crosslinked LDPE as a function of crosslinking time at various temperatures for 1-phr silane-grafted film samples with thicknesses of 0.53 and 1.02 mm, respectively. As can be seen in Figures 2 and 3, the gel content increases with increasing time, and, at 100°C of water temperature, up to around 40% of gel content can be reached for 38 h of crosslinking. The gel content is linearly related to the crosslinking time up to 38 h if the reaction temperature is 80°C and over for the sample of 0.53 mm in thickness (Fig. 2) but is 90°C and over for the sample of 1.02 mm in thickness (Fig. 3). This implies that the relationship between gel content and crosslinking time is dependent on the thickness and the content of crystalline component of the silane-grafted LDPE sample.

Figures 4, 5, and 6 show plots of gel contents of 0.53-mm thick LDPE samples with various silane

grafting extents as functions of crosslinking times at 80, 90, and 100°C, respectively. As can be seen in Figure 4, for 80°C, the gel content is linearly related to the crosslinking time up to 38 h for samples grafting with 1, 3, and 5 phr silane. The slope of a plot in Figure 4, that is, the crosslinking rate of a silane-grafted sample, is in the order of 5-phr > 3-phr > 1-phr silane-grafted sample. At this temperature (80°C) and for 38 h of crosslinking, the 5-phr silane-grafted sample leads to the highest gel content (around 40%) among the three samples with different silane grafting extents. As can be seen in Figures 5 and 6, for 90 and 100°C, the gel contents are not linearly related to the crosslinking times throughout the study range of 0–38 h for samples with 3 and 5 phr of silane graftings. The relations of gel contents and crosslinking times for these two samples can be fitted with two different slopes of straight lines connecting at a point falling, as seen in plots B and C of Figures 5 and 6, in the range of 30–40% of gel content. The initial crosslinking rates (i.e., slopes of the initial linear portion of the fitted straight lines) of samples at these two temperatures (90 and 100°C) also follow the same order as that at 80°C, that is, $r_{5 \text{ phr}} > r_{3 \text{ phr}} > r_{1 \text{ phr}}$.

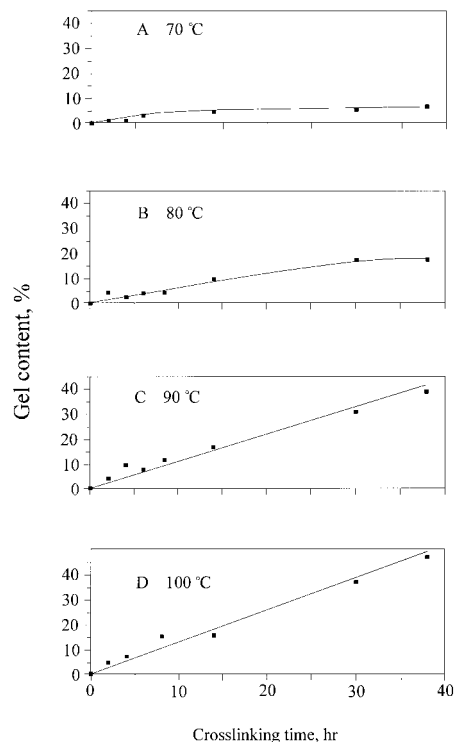


Figure 3 Plots of the gel contents of the 1-phr silane-grafted LDPE film samples with 1.02 mm in thickness as a function of crosslinking time at (A) 70°C, (B) 80°C, (C) 90°C, (D) 100°C.

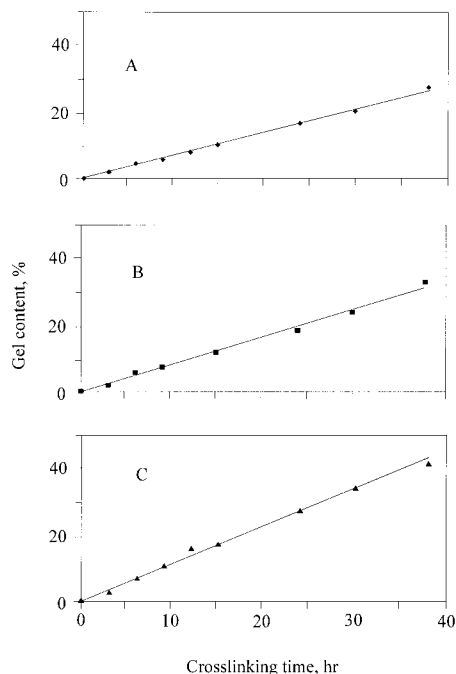


Figure 4 Plots of the gel contents of the (A) 1-phr, (B) 3-phr, and (C) 5-phr silane-grafted LDPE film samples with 0.53 mm in thickness as a function of crosslinking time at 80°C.

Table I lists initial crosslinking rates (%/h, determined from slopes of the initial linear portions of the fitted straight lines in plots of Figs. 2–6) at various crosslinking temperatures for two different thicknesses of samples with various silane grafting extents. The amount of silane used for samples being 0.53-mm thick includes 1, 3, and 5 phr and for samples being 1.02-mm thick is 1 phr. Table II lists the gel contents of those samples in Table I after crosslinking for 38 h at various temperatures. As listed in Table II, the 0.53-mm thick sample with 5 phr silane grafting gives higher gel contents than those samples with 3 or 1 phr silane grafting after crosslinking for 38 h at temperatures studied. Gel content of as high as 65.8% for the 0.53-mm thick sample with 5 phr silane grafting is obtained after crosslinking for 38 h at 100°C.

DISCUSSION

Figure 7 shows DSC thermograms of LDPE (thermogram A), the 1-phr silane-grafted LDPE (thermogram B), the silane-grafted water-crosslinked LDPE having around 30% of gel content (thermogram C), and the silane-grafted water-crosslinked

LDPE having around 55 wt % of gel content (thermogram D). As can be seen in thermograms A–C of Figure 7, the peak temperatures for silane-grafted and silane-grafted water-crosslinked LDPEs slightly shift to lower values compared with that for LDPE. For the sample containing around 55% gel content, the corresponding thermogram (thermogram D in Fig. 7) exhibits multiple melting peaks with the main peak temperature surprisingly shifting to a higher value. From thermograms C and D of Figure 7, the morphology of the sample containing a low gel content (around 30%) is, apparently, quite different from that containing a high gel content (around 55%). This significantly different morphology can also be demonstrated by polarized optical micrographs (POM), as shown in Figure 8.

In Figure 8, crystal formations can be observed for all four samples. Because samples for the POM characterization are prepared by casting from xylene, crystal morphologies as exhibited in polarized optical micrographs A and B for LDPE and the silane-grafted LDPE, respectively, represent morphologies of the bulk of these samples due to complete dissolution of samples in xylene at elevated temperature. Morphologies as exhib-

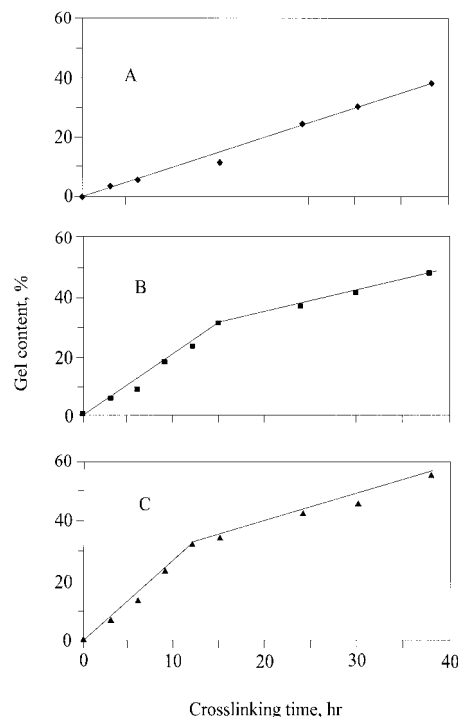


Figure 5 Plots of the gel contents of the (A) 1-phr, (B) 3-phr, and (C) 5-phr silane-grafted LDPE film samples with 0.53 mm in thickness as a function of crosslinking time at 90°C.

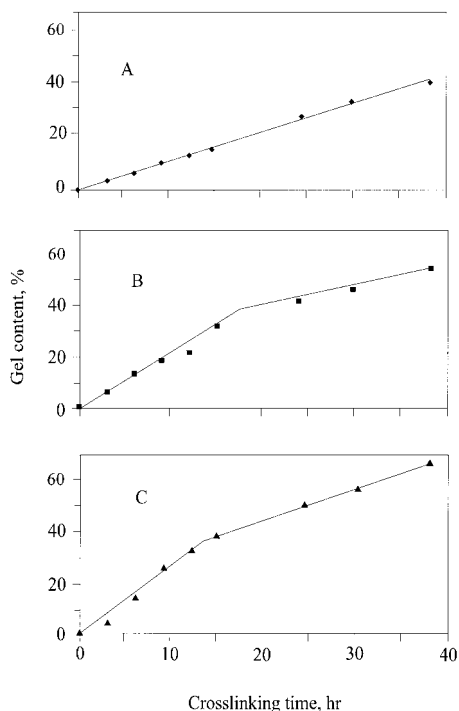


Figure 6 Plots of the gel contents of the (A) 1-phr, (B) 3-phr, and (C) 5-phr silane-grafted LDPE film samples with 0.53 mm in thickness as a function of crosslinking time at 100°C.

ited in micrographs C and D for the silane-grafted water-crosslinked LDPEs, however, represent morphologies of only the soluble component of the samples in xylene. As can be seen in micrograph A of Figure 8 for LDPE, there are many spherulites with a variety of sizes impinging on each other. The silane-grafted LDPE results in much decreased spherulite size with much less perfec-

Table I Initial Crosslinking Rates (%/h) at Various Crosslinking Temperatures for Two Different Thicknesses of Silane-Grafted LDPE Samples

Crosslinking Temperature	Thickness 0.53 mm			Thickness 1.02 mm
	1 phr	3 phr	5 phr	1 phr
60°C	0.35	—	—	—
70°C	0.62	—	—	0.31
80°C	0.71	0.8	1.09	0.57
90°C	0.95	2.01	2.67	0.89
100°C	1.15	2.04	2.7	1.20

The amount of silane used for the 0.53-mm thick silane-grafted LDPE samples includes 1, 3, and 5 phr and for the 1.02-mm thick samples is 1 phr.

Table II The Gel Contents (%) of Two Different Thicknesses of Silane-Grafted LDPE Samples after Crosslinking for 38 h at Various Temperatures

Crosslinking Temperature	Thickness 0.53 mm			Thickness 1.02 mm
	1 phr	3 phr	5 phr	1 phr
60°C	5.7%	—	—	—
70°C	10.8%	—	—	5.1%
80°C	27.7%	32.2%	39.5%	17.2%
90°C	38.0%	47.1%	55%	38.4%
100°C	40.1%	54%	65.8%	44.7%

The amount of silane used for the 0.53-mm thick silane-grafted LDPE samples includes 1, 3, and 5 phr and for the 1.02-mm thick samples is 1 phr.

tion (micrograph B of Fig. 8). This suggests that the silane graftings, on the one hand, act as a nucleating agent in crystallization of the sample

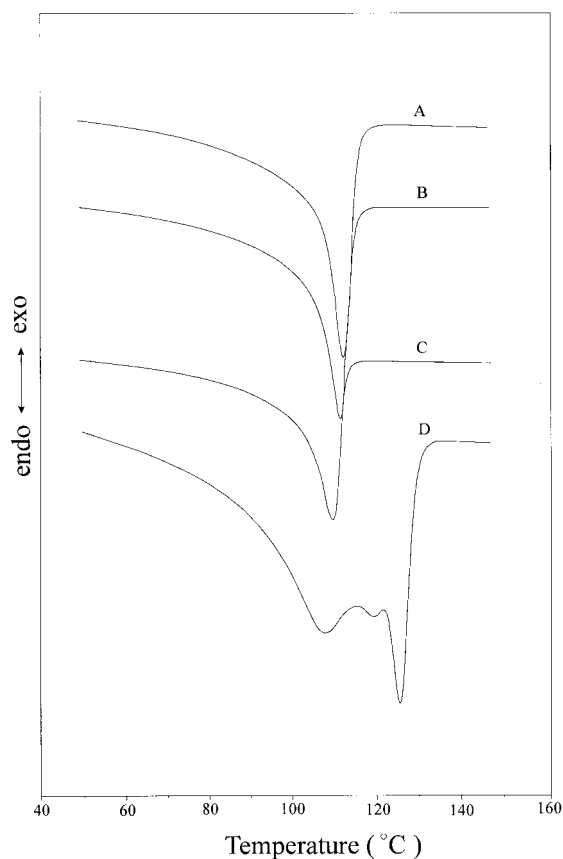


Figure 7 DSC thermograms of (A) LDPE, (B) the 1-phr silane-grafted LDPE, (C) the silane-grafted water-crosslinked LDPE having gel content of about 30 wt %, and (D) the silane-grafted water-crosslinked LDPE having gel content of about 55 wt %.

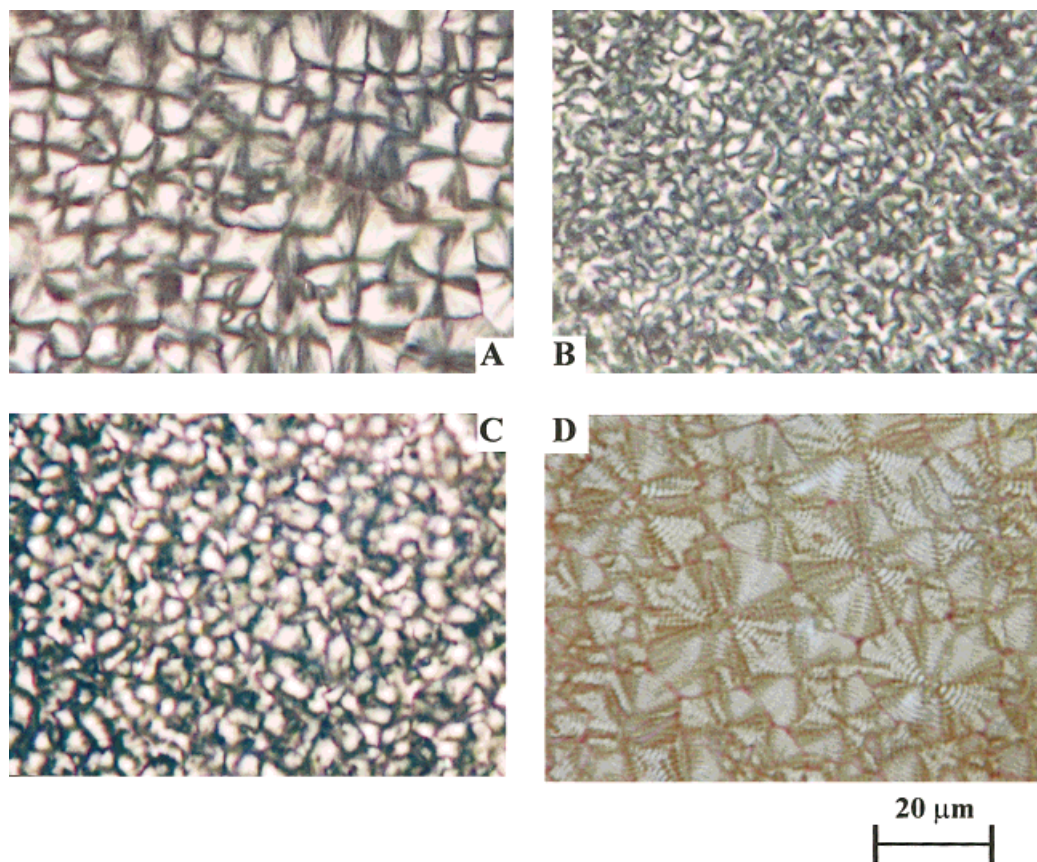


Figure 8 Polarized optical micrographs for (A) LDPE, (B) the 1-phr silane-grafted LDPE, (C) the silane-grafted water-crosslinked LDPE having gel content of about 30 wt %, and (D) the silane-grafted water-crosslinked LDPE having gel content of about 55 wt %.

leading to a decreased spherulite size and, on the other hand, introduce structural irregularity onto LDPE molecules leading to low perfection in the growth of spherulites. The sizes of spherulites increase with increasing degrees of crosslinking, as can be seen in micrographs C and D of Figure 8. The spherulite size for the soluble component of the sample containing about 55% of gel content is even bigger than that for LDPE. This suggests that the molecularly structural regularities of the soluble components in these samples increase with increasing degrees of crosslinking. This is because the silane grafting reactions (and thus crosslinking reactions thereafter) occur mostly with those molecules with branches, that is, molecules with tertiary carbons.⁷ As the degree of crosslinking increases, the content of branched or silane-grafted molecules (or the content of molecules with a low structural regularity) decreases in the soluble component of the sample. In other words, the concentration of molecules with a low content of branches or silane grafts in the soluble component of the sample increases with increas-

ing degree of crosslinking. The POM micrographs in Figure 8, thus, can be used to explain the finding of crystallization enhancement of LDPE upon silane grafting and crosslinking as demonstrated by DSC data in Figure 7(D).

Based on discussion above, the question of why the gel content is not linearly related to the crosslinking time for samples having 3 and 5 phr silane grafting (Figs. 5 and 6) can be answered as follows: the diffusion of water in the sample is governed by, in addition to the content of crystalline component (this effect is discussed later in this paper), the perfection or size of crystallite of the sample. As discussed previously, the perfection or size of crystallite in a sample increases with increasing gel content in the sample. As the gel content in the sample is higher than a certain value that is found to fall in the range of 30–40% as observed in Figures 5 and 6, the perfection or size of crystallite in the sample is enhanced, as demonstrated by both DSC and POM. This enhanced perfection or size of crystallite gives a lower diffusion rate of water and, thus, a lower

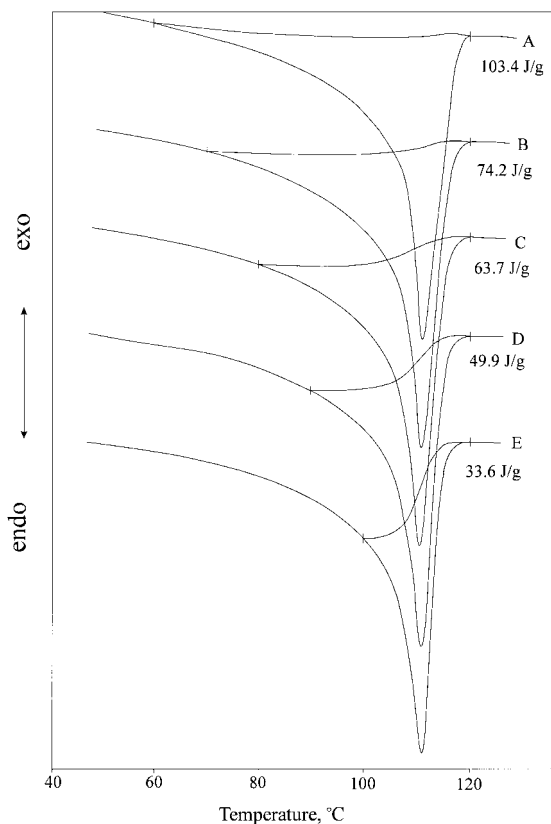


Figure 9 DSC thermograms with the area integration of the endothermic peak from (A) 60°C, (B) 70°C, (C) 80°C, (D) 90°C, and (E) 100°C to 120°C for the 1-phr silane-grafted LDPE sample.

crosslinking rate leading to a lower slope of the plot in Figures 5 and 6 for the later stage of crosslinking reaction.

In Figure 7, it is observed that the endothermic melting peak for the silane-grafted LDPE sample starts at around 60°C, which is much lower than its main melting temperature (T_m) at around 110°C. In other words, the sample starts to melt at around 60°C, and the melting increases with increasing temperatures until around 110°C before which the content of the crystalline component decreases with increasing temperatures. The content of the crystalline component in a sample at a temperature in the range of 60°C– T_m can be determined by the integration of the endothermic peak area (i.e., the heat of fusion) from the temperature to 120°C, as shown in Figure 9. The calculation of the content of crystalline component in a sample is performed by dividing the heat of fusion of the sample by that of the polyethylene crystal. The heat of fusion of the polyethylene crystal is 281 J/g.¹⁴ The contents of the crystalline component in the 1-phr silane-grafted

LDPE sample at 60, 70, 80, 90, and 100°C are, thus, 36.8, 26.4, 22.7, 17.8, and 12.0 wt % calculated from temperature ranges of 60–120, 70–120, 80–120, 90–120, and 100–120°C, respectively.

Diffusion of water in the amorphous domain is believed to be faster than that in the crystalline domain. This suggests that the crosslinking rate in the amorphous domain is faster than that in the crystalline domain. Having a higher content of the amorphous component in a silane-grafted LDPE sample at a higher temperature (Fig. 9), a faster crosslinking rate for the sample can be obtained (Figs. 2–6), and a longer time can be reached for the sample to maintain a linear relationship between the gel content and the crosslinking time (Figs. 2 and 3).

The effect of the crosslinking temperature on the gel content of the water-crosslinked sample is complicated, because the temperature affects not only the content of the crystalline component (Fig. 9) and, thus, the diffusion rate of water but also the subsequent hydrolysis and condensation rates of the silyl trimethoxy moiety. Figures 2–6 show that the gel contents of the samples conducted for a certain crosslinking time increase with increasing temperatures. It is, thus, demonstrated that the diffusion rate of water and the subsequent hydrolysis and condensation rates of the silyl trimethoxy moiety increase with increasing temperatures.

From Figures 2–6, the fitted curves on plots of the gel content vs. the crosslinking time are considered to be linear in the initial hours. The slopes of these initial linear portions of lines are used to determine the crosslinking rates of samples. Table I lists crosslinking rates of samples studied at various temperatures. For the 1-phr silane-grafted LDPE samples, it is found that the crosslinking rates of the thinner sample are higher than those of the thicker sample at temperatures of 90°C and below. The crosslinking rates at 100°C are almost the same within experimental error for both samples in different thickness. The difference of the crosslinking rates between these two samples increases as the temperature decreases. This suggests that the control variable in the crosslinking process is the diffusion of water in the sample at low temperatures. In other words, the diffusion of water is the rate-determining step in the crosslinking process at low temperatures. The effect of this diffusion control on the crosslinking rate appears to be insignificant at 100°C, at which the content of crystalline component is low and the chemical reaction

rate is high and, thus, the chemical reaction control dominates the crosslinking process. This chemical reaction control in the crosslinking process is also evidenced from the crosslinking rates of both 3-phr and 5-phr silane-grafted LDPE samples at 90 and 100°C (Table I). As can be seen in Table I, insignificant differences in crosslinking rates at 90 and 100°C are demonstrated for both samples due to much higher crosslinking rates at these temperatures compared with crosslinking rates for the 1-phr silane-grafted samples.

In Table II lists gel contents of samples after crosslinking for 38 h at various temperatures. As can be seen in Table II, the gel contents of samples increase with increasing temperatures. For the 1-phr silane-grafted samples, the gel content of the thinner sample is higher than that of the thicker sample at temperatures below 90°C. For 38 h of crosslinking at 90 and 100°C, the effects of thickness of samples on the gel contents appear to be insignificant because the crosslinking reactions are completed before the crosslinking process is ended at a time of 38 h. For the 0.53 mm-thick samples, the gel contents increase with increasing silane-grafting extents at any crosslinking temperature studied. This is consistent with FTIR data, as shown previously, where the extents of silane grafting reactions are found to increase with increasing amount of silane used for the grafting reactions. Therefore, among many factors, the extent of silane grafting reaction is an important factor to the highest achievable gel content of sample.

Figure 10 shows plots of crosslinking rates as functions of contents of crystalline component for two different thicknesses of samples. The crosslinking rates are inversely proportional to the contents of crystalline component for the samples. This is because the diffusion of water decreases with increasing content of the crystalline component in the sample. The crosslinking rate for the thinner sample is slightly less dependent on the content of crystalline component than that for the thicker one. Figure 11 shows plots of the gel contents of the two different thicknesses of samples after crosslinking for 38 h as functions of the contents of crystalline component. The gel contents are also inversely proportional to the contents of crystalline component for the samples. The gel content of the thinner sample is also slightly less dependent on the content of crystalline component than that for the thicker one. Figures 10 and 11 suggest that the crosslinking reactions occur mainly in the amorphous domain of the sample.

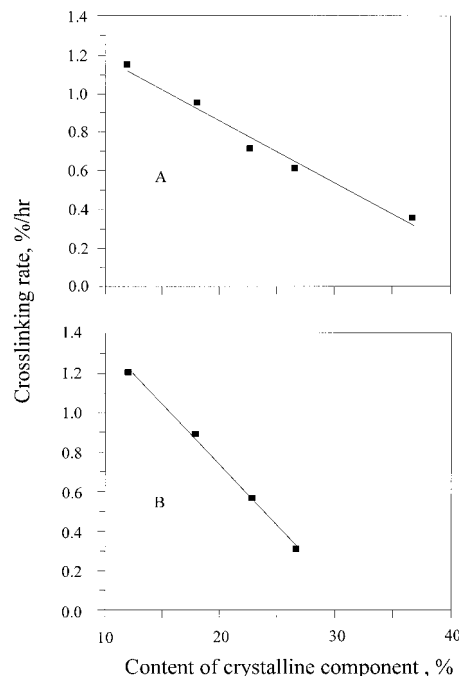


Figure 10 Plots of the crosslinking rates as a function of the content of crystalline component for the 1-phr silane-grafted LDPE samples with (A) 0.53 mm and (B) 1.02 mm thickness.

To investigate the diffusion behavior of water in LDPE, a sorption experiment in boiled water is performed for the 0.53 mm-thick sample. Negligible weight change, however, is found for the sample after 40 h of sorption experiment in boiled water. This represents that the diffusion of water in LDPE is negligible at even 100°C. To investigate the effect of water concentration on the crosslinking rate of sample, crosslinking reactions are performed in an oven of constant humidity at 80°C. Table III lists the gel contents of the 0.53 mm-thick sample after crosslinking for various times at 80°C under various relative humidities. For a certain time, it is found that the gel content increases with increasing relative humidity. In other words, the crosslinking reaction rate increases with increasing concentration of water. Consequently, the crosslinking reaction proceeds in such a way that the hydrolysis and subsequent condensation reactions of the silyl trimethoxy groups with water begin initially on the surface of the film sample followed by diffusion of the liberated water from the previous condensation reactions into the sample. The direction and driving force of the water diffusion into the sample are apparently (Table III) dependent on the concentration of water. The higher concentration of water can give the higher driving force of the water

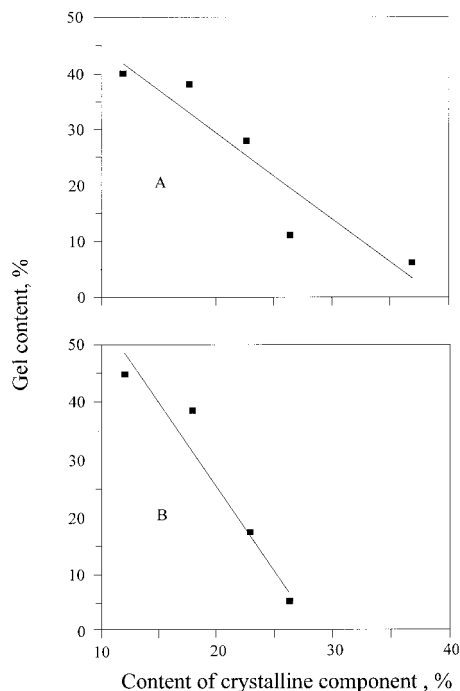


Figure 11 Plots of the gel contents as a function of the content of crystalline component for the 1-phr silane-grafted LDPE samples with (A) 0.53 mm and (B) 1.02 mm thickness.

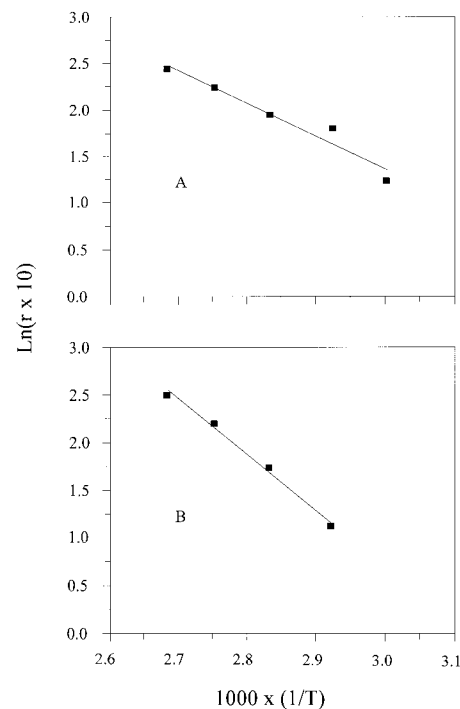


Figure 12 Plots of logarithmic crosslinking rates as a function of reciprocal absolute temperature for the 1-phr silane-grafted LDPE samples with (A) 0.53 mm and (B) 1.02 mm thickness.

diffusion into the sample. The water diffused into the surface can then induce the next hydrolysis and condensation reactions of the silyl trimethoxy groups and lead to crosslinking of the sample. With this reaction scheme, a series of crosslinking reactions proceeds continuously until all silyl trimethoxy groups in the amorphous domain are completely consumed.

Figure 12 shows plots of logarithmic crosslinking reaction rates for the two different thicknesses of 1-phr silane-grafted film samples as a function of the reciprocal absolute temperature. The logarithmic crosslinking rates are found to be linearly related to the reciprocal absolute temper-

atures. The plots can thus be described by the Arrhenius equation that follows.

$$r = A \exp(-E/RT) \quad (3)$$

where r is the crosslinking rate (%/h), A is a preexponential constant, T is the absolute temperature, R is the gas constant, and E is the overall activation energy for the crosslinking reactions. Thus, the overall activation energies are the minus slopes of the fitted lines in the plots multiplied by the gas constant. The overall activation energies of the crosslinking reactions are thus 28.8 and 46.9 kJ/mol for samples of 0.53 and 1.02 mm in thickness, respectively. The overall activation energy is apparently dependent on the thickness of sample. The crosslinking reaction of the thinner sample has a smaller overall activation energy, and is thus less temperature dependent than that of the thicker one. As noted previously, the crosslinking reactions of the sample include the diffusion of water, the hydrolysis of the silyl trimethoxy groups by the water, and the subsequent condensation of the formed silanol groups to form crosslinks. The diffusion of water has been previously demonstrated to be the rate-

Table III The Gel Contents (%) of the 0.53 mm-Thick Sample after Crosslinking at 80°C in Three Different Relative Humidity (RH) Environments for 14, 30, and 38 h

Crosslinking Time	RH 35%	RH 77%	RH 100%
14h	0.4%	8.0%	10.2%
30h	1.7%	16.9%	21.8%
38h	1.7%	18.9%	27.7%

determining step in the crosslinking reactions, and to be dependent on both the thickness and the content of crystalline component of the sample. These demonstrations support the findings that the overall activation energy of the crosslinking reactions is dependent on thickness of the sample, and the crosslinking reaction of the thicker sample is more temperature dependent than that of the thinner one.

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