Thermal Properties of Silane-Grafted Water-Crosslinked Polyethylene

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ABSTRACT: Vinyl trimethoxysilane grafting reactions of low-density polyethylene (LDPE) were performed in an extruder, followed by crosslinking with boiled water. The thermal properties of both silane-grafted and silane-grafted water-crosslinked LDPE were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC data showed that the silane grafts on the LDPE molecules were thermal stable in the absence of moisture under 130°C under which the silane-grafted LDPE could be processed or recycled. The silane grafts on the LDPE molecules reduced the melting point of LDPE and gave rise to an endotherm shoulder at about 85°C. TGA data showed that the decomposition temperature of the silane-grafted LDPE was much higher than that of LDPE. It was demonstrated that the cause of the increase in the decomposition temperature was not due to the silane grafts but due to the peroxide-induced crosslinking reactions during the silane grafting reactions performed in an extruder. Silane-grafted water-crosslinked LDPE displayed multiple melting behavior resulting from phase separation during crosslinking of LDPE with water. The phase separation gave rise to two melting points, including one at about 94°C, and the other at about 107°C. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1075–1082, 1998

Key words: polyethylene; grafting reactions; crosslinking reactions; thermal properties

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 that can provide crosslinking capability, such as the kind one finds in typical thermosetting resins. Hence, the crosslinking must be induced by the incorporation of another component. 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 are capable of extracting a hydrogen from the polyethylene backbone, thus transferring the free radical site to the polyethylene. With this accomplished, 2 polyeth-

ylene chains can crosslink together. 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 reactions of the silane grafts 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 through hydrolyzations of the methoxysilane groups with water, followed by condensation of the formed hydroxyl groups. The mechanisms leading to coupling between the methoxysilane groups in the silane-grafted polyethylene are believed to be as follows.[2]

$$(1)$$

$$(2)$$
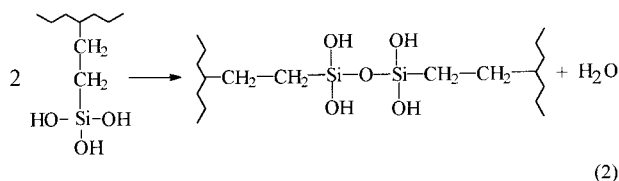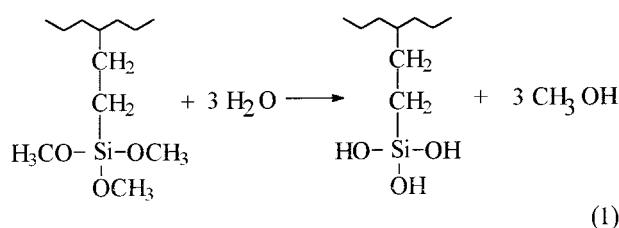
The crosslinkable silane-grafted polyethylene can be processed in any modern thermoplastic extruder. Before used for processing, the silane-grafted polyethylene should be stored in a cool and dry place away from direct sunlight and moisture because moisture can cause crosslinking of the material at elevated temperatures. Di-*n*-butyltin dilaurate, as a catalyst, is normally incorporated during processing of the silane-grafted

polyethylene in order to speed up the crosslinking reactions of the material with moisture or water.

There have been some articles[3–9] published on the crosslinking of polyethylene. Sen and colleagues[3,4] reported some kinetics data, studied by differential scanning calorimetry (DSC), X-ray diffractometry (XRD) and dynamic mechanical analysis (DMA), on silane grafting and moisture crosslinking of polyethylene and ethylene propylene rubber. Kao and Phillips[5] reported the crystallinity and other structural information, using DSC and XRD, of low-density polyethylene (LDPE) crosslinked by dicumyl peroxide. Hjertberg and colleagues[2] and Bullen and colleagues[6] studied the crosslinking reactions of ethylene–vinyl trimethoxysilane copolymers. The article by Bullen and coworkers,[6] crosslinking of the copolymer during high-temperature melt processing, was investigated using melt rheological and infrared spectroscopic techniques, whereas in the articles by Hjertberg and colleagues[2] and Palmlof and colleagues,[7] the kinetics of crosslinking of the copolymer when reacted with water was followed by measuring gel content and by determination of the content of different groups (—Si—OCH$_3$, —Si—OH, and —Si—O—Si—) using Fourier transform infrared (FTIR) spectroscopy. Narkis and coworkers[8] presented studies on 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. Turcsanyi and coworkers[9] studied structure–property relationships of silane-modified and crosslinked linear polyethylene using DSC and thermomechanical analysis (TMA). The aim of this work was to study the thermal properties of both silane-grafted and silane-grafted water-crosslinked LDPE. DSC and thermogravimetry (TGA) were used for this study.

EXPERIMENTAL

Materials

All materials were used as received. LDPE (C7100) was received from Asia Polymer Corporation (Taipei, Taiwan) with a melt index (ASTM D1238) of 7.3 and a density (ASTM D1505) of 0.9175 g/cm^3. The peroxide used was dicumyl peroxide supplied by Aldrich Chemical Company (Milwaukee, WI). The silane used was vinyl tri-

Table I Sample Designations and Compositions

Sample Designation	Sample Composition			
	LDPE (Parts)	Peroxide (phr)	Silane (phr)	Catalyst (phr)
A1	100	0.15	2	—
A2	100	0.10	2	—
A3	100	0.05	2	—
AB1	100	0.15	2	0.05
AB2	100	0.10	2	0.05
AB3	100	0.05	2	0.05

methoxysilane supplied by Tokyo Kasei Kogyo Co (Tokyo, Japan). The catalyst was di-*n*-butyltin dilaurate supplied by Strem Chemicals (Newburyport, MA).

Sample Preparation

LDPE pellets were mixed with the peroxide and the silane in a blender under dry nitrogen at 75°C until the mixture became dry. For those samples which were investigated on the effects of the catalyst, the catalyst was added into the blender during the mixing. This process normally took 30 min and had been determined to be effective in providing uniform silane and peroxide dispersion on the surface or in the amorphous fraction of LDPE pellets. All these prepared mixtures were subsequently compounded in an extruder (single screw of 50 mm in diameter; *L/D,* 19; compression ratio, 3.5) at 20 rpm and high temperatures ranging from 170°C at the feed zone to 190°C at the metering zone to 210°C at the die zone of the extruder. The silane grafting reactions occurred during the compounding in the extruder. The concentration of the silane used was fixed at 2 phr (part of reagent per hundred parts of LDPE) for all samples, while the concentration of the catalyst, if used, was 0.05 phr. The concentration of peroxide was varied at 0.05, 0.1, and 0.15 phr with respect to LDPE. Table I shows sample designations and their compositions. For crosslinking, the silane-grafted LDPE samples, as shown in Table I, were reacted with boiled water for various times. The designations for samples having conducted crosslinking were, for example, A1Cn, A2C6, AB2C4, and AB3C2 corresponding to samples A1, A2, AB2, and AB3 with crosslinking in boiled water for *n*, 6, 4, and 2 h, respectively.

Analysis

FTIR (Bio-Rad FTS155) was used to qualitatively demonstrate the grafting reactions of the silane onto LDPE. The samples for FTIR measurements were films made by using a hot press at 130°C. DSC (TA Instruments, New Castle, DE, DSC 2010) was used to analyze the thermal stability and melting behavior of samples in terms of changes of melting endotherms of the samples. The samples for DSC measurements were 5 to 15 mg encapsulated in aluminum pans at a heating, or cooling, for some cases, of 20°C/min under nitrogen. TGA (TA Instruments TGA 2050) was used to analyze the thermal stability of samples in terms of the decomposition temperatures of the samples. The samples for TGA measurements were 5 to 15 mg heated from room temperature to 900°C at a heating rate of 20°C/min under nitrogen.

RESULTS AND DISCUSSION

Silane-Grafted Polyethylene

Figure 1 shows FTIR spectra of LDPE before [spectrum (A)] and after reaction with the peroxide (spectrum B) and the silane [spectrum (C)]. In comparison between these spectra, the peroxide [spectrum (B)] did not give rise to any change in the LDPE spectrum (spectrum A). The silane [spectrum (C)], however, gave rise to at least 3 more peaks at 789, 1092, and 1192 cm^{-1}. Thus, the silane grafting reactions had occurred since the peaks at 1092 and 1192 cm^{-1} were assigned to the functional group Si—OCH$_3$.[2,3,10,11]

LDPE has a branched structure. The peak at 1378 cm^{-1} due to —CH$_3$ bending vibrations[11] in
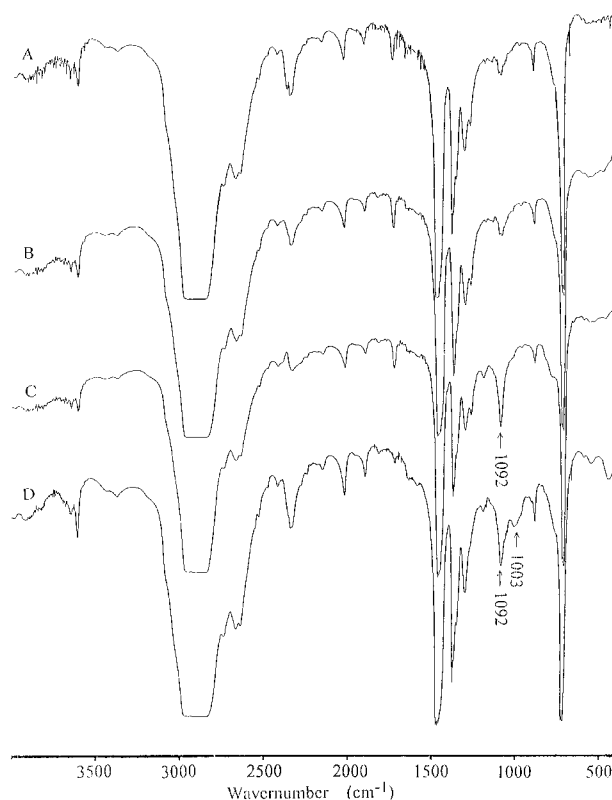
Figure 1 FTIR spectra of (A) LDPE, (B) LDPE reacted with 0.15-phr dicumyl peroxide, (C) LDPE reacted with 0.15-phr dicumyl peroxide and 2-phr vinyl trimethoxysilane, and (D) LDPE reacted with 0.15-phr dicumyl peroxide and 2-phr vinyl trimethoxysilane, followed by crosslinking with boiled water for 4 h.

FTIR spectra [spectrum (A) in Fig. 1] provides evidence of the branched structure of LDPE. In DSC thermogram [trace (A) in Fig. 2] of LDPE, an endothermic peak appeared during heating. The endotherm began to appear at about 70°C due to the branched structure in LDPE. Traces (B)–(D) in Figure 2 displayed the effects of the heating scans on the endothermic peak of sample A1. Trace (B) in Figure 2 demonstrated that the silane-grafted sample A1 had an endothermic shoulder at about 85°C. The shoulder, however, disappeared during the second and third heating scans perhaps due to a homogenious mixing of the silane grafts and the hydrocarbon branches after the first heating scan. An endothermic shoulder was not observed for samples A2 and A3, as shown in Figure 3, in which all DSC traces were obtained from the first heating scan. The cause for the disappearance of the endothermic shoulders for samples A2 and A3 was perhaps due to a less amount of dicumyl peroxide used and, thus, a

less extent of silane grafting for these samples than for A1. The melting temperatures of samples A1, A2, and A3 during 3 heating scans are listed in Table II. The melting temperatures insignificantly varied with the heating scans from room temperature to 130°C under nitrogen. This suggests that the silane grafts in the absence of moisture were thermal stable below 130°C, under which the silane-grafted LDPE could be recycled without a significant change in melting behavior. The melting temperature of A1 from the first heating scan was 104.7°C and was 3.0°C lower than that of LDPE. The decrease in the melting temperature of A1 was due to the silane grafts, which reduced the structure regularity of LDPE. The melting temperatures of A2 and A3 were slightly higher than that of A1, implying that the extent of silane grafting of A2 and A3 were lower than that of A1.

Figure 4 shows TGA data of LDPE, A1, and A2. If the peak of the first derivative curve of a TGA trace in Figure 4 was regarded as the decomposition temperature, the decomposition temperatures of A1 and A2 were 467.8 and 479.5°C, respectively, which were much higher than 425.7°C for LDPE. The decomposition temperature of A3 was 475.6°C (not shown in Fig. 4). In comparison between silane-grafted LDPEs, the cause for the lowest decomposition temperature for A1 was probably due to the leftover of dicumyl peroxide after the grafting reactions performed in the extruder. The leftover of the peroxide resulted in generation of free radicals and subsequent chain scission of the LDPE molecules during TGA measurements. The cause for the relatively low decomposition temperature for A3 compared to A2 was due to less concentration of dicumyl peroxide used for sample A3. Less concentration of the peroxide used for sample A3 led to less peroxide crosslinking of LDPE molecules during the silane grafting reactions and, thus, led to lower decomposition temperature. The effects of the catalyst on the decomposition temperatures (not shown) and melting temperatures (Table II) of the silane-grafted samples were found to be insignificant.

The effects of the silane grafts on the decomposition temperatures were demonstrated using the following 2 samples. One of these samples had the composition of 100 parts of LDPE and 0.15 phr of DCP. The other one had 100 parts of LDPE and 0.15 phr of DCP and 2 phr of silane. These 2 samples were prepared using an extruder with the same operating temperatures as previously described. The TGA traces of these 2 samples
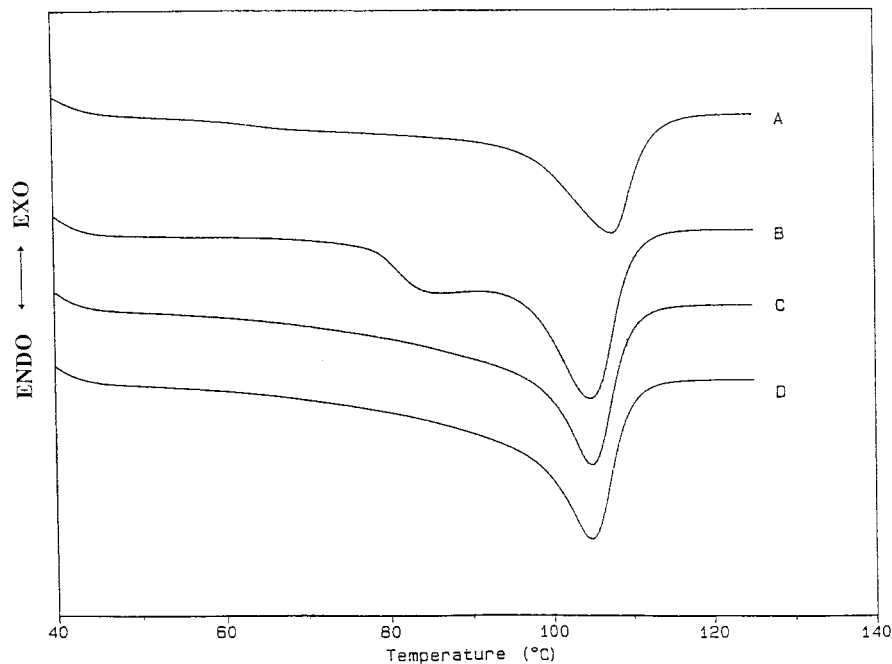
Figure 2 DSC traces of (A) LDPE from the first heating scan, (B) A1 from the first heating scan, (C) A1 from the second heating scan, and (D) A1 from the third heating scan, at a rate of 20°C/min under nitrogen.

heated at 20°C/min under nitrogen were totally overlapped from room temperature to 900°C. The TGA data suggested that condensation reactions of the silane grafts did not occur during the TGA heating and, thus, the silane grafts were insensitive to heat. The TGA results were consistent
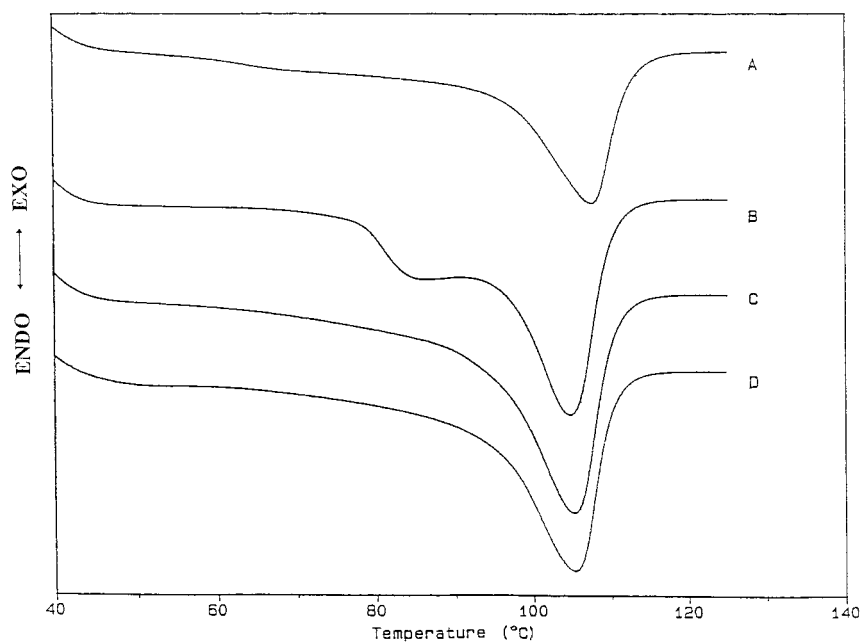

Figure 3 DSC traces obtained from the first heating scan at a rate of 20°C/min under nitrogen for (A) LDPE, (B) A1, (C) A2, and (D) A3.

Table II Melting Temperatures of First, Second, and Third Heating Scans from DSC Measurements at a Rate of 20°C/min Under Nitrogen

Sample	1st Heating (°C)	2nd Heating (°C)	3rd Heating (°C)
LDPE	107.7	107.4	107.5
A1	104.7[a]	104.9	104.7
A2	105.3	105.4	105.2
A3	105.4	105.3	105.6
AB3	104.6	104.5	104.5

[a] With an endotherm shoulder at 85°C.

with DSC data in terms of thermal stability of the silane grafts.

Silane-Grafted and Water-Crosslinked Polyethylene

Spectrum (D) in Figure 1 demonstrates that condensation reactions of the silane grafts with water occurred because the peak at 1003 cm^{-1} was assigned to the Si—O—Si group.[2,3,10,11]

Figure 5 displays DSC thermograms of LDPE, A1, A1C2, A1C4, A1C6, and A1C8. Multiple melting behavior was found for the water-crosslinked polyethylene [traces (C)–(F)]. The behavior displayed 2 melting points: one at about 107.0°C; the other at about 94.0°C. These 2 melting points did not change significantly as the crosslinking time increased. Similar melting behavior was also found for water-crosslinked samples A2Cn and A3Cn. These 2 melting points were corresponding to 2 crystalline structures, including sol and gel fractions, and these 2 structures were excluded by each other. The melting point (T_{m2}) at about 107.0°C was due to the sol fraction, while the other (T_{m1}) at about 94.0°C was due to the gel fraction. Table III lists melting points from the first heating scan for samples AB1Cn, AB2Cn, and AB3Cn, which have crosslinked with boiling water for n h. The differences of T_{m2} and T_{m1} are listed in the fourth column of Table III. For samples AB2Cn and AB3Cn, as expected, the differences enlarged as the crosslinking time increased because the increase of crosslinking time led to an increase of degree of crosslinking and, thus, a further phase separation of the 2 different crystalline structures. Thus, as the crosslinking time increased, the melting point of the gel fraction decreased, whereas the melting point of the sol fraction increased. The increase of the melting point of the sol fraction was limited to about 108°C, which was close to the melting point of LDPE. For crosslinked sample AB1Cn, the multiple melting behavior was different from those for crosslinked AB2Cn and AB3Cn. An endo-
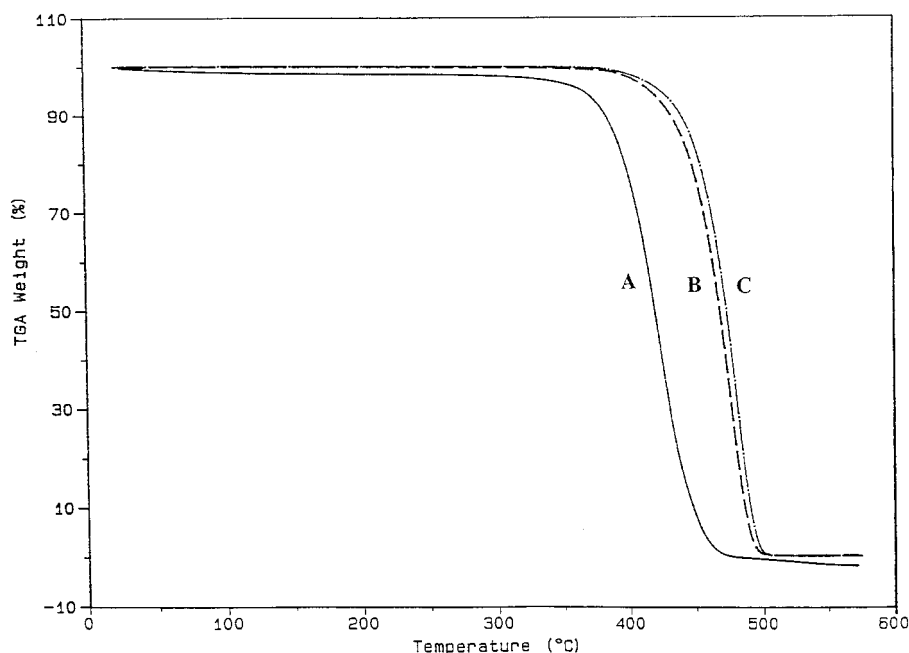

Figure 4 TGA traces of (A) LDPE, (B) A1, and (C) A2, at a heating rate of 20°C/min under nitrogen.
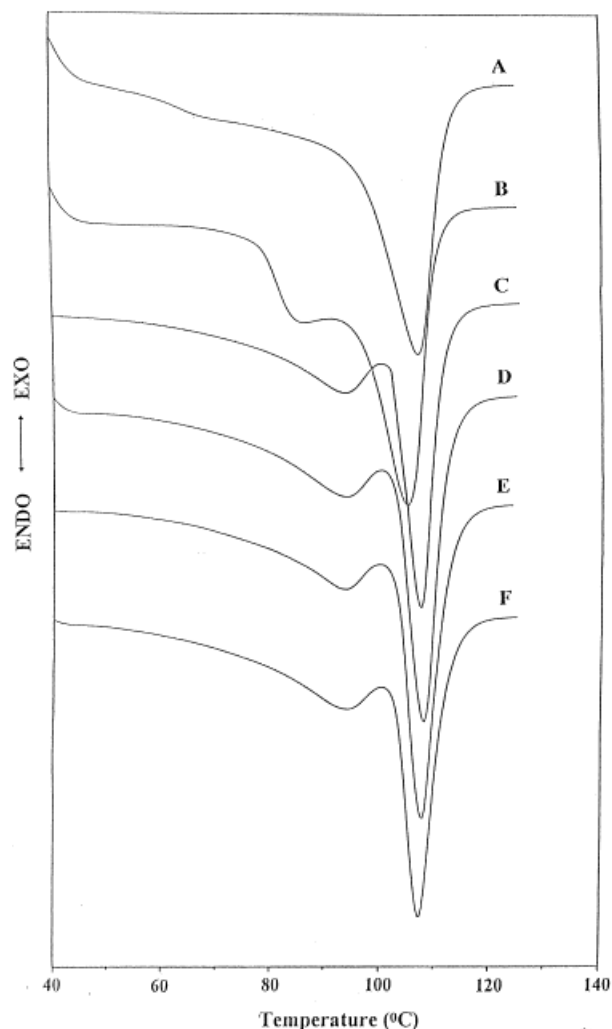
Figure 5 DSC traces obtained from the first heating scan at a rate of 20°C/min under nitrogen for (A) LDPE, (B) A1, (C) A1C2, (D) A1C4, (E) A1C6, and (F) A1C8.

Table III   Melting Temperatures of LDPE and Various Water-Crosslinked LDPE Obtained from DSC Measurements

Sample	T_{m1} (°C)[a]	T_{m2} (°C)	ΔT_m (°C) $(=T_{m2} - T_{m1})$
LDPE	—	107.7	—
AB1C2	85.0[b]	104.3	19.3
AB1C4	85.0[b]	104.4	19.4
AB2C2	94.5	106.6	13.1
AB2C4	94.0	107.5	13.5
AB2C6	94.0	107.7	13.7
AB2C8	93.0	108.1	15.1
AB2C10	92.0	107.8	15.8
AB2C12	92.0	108.5	16.5
AB3C2	95.0	106.8	11.8
AB3C4	93.8	106.9	13.1
AB3C6	93.8	107.8	14.0
AB3C8	93.5	107.8	14.3

[a] Small endotherm peaks.
[b] Endotherm shoulders.

nificant in AB1Cn and, thus, led to insignificant phase separation. The DSC data of the crosslinked sample AB1Cn is consistent with that of A1 from which an endotherm shoulder was also observed at 85°C. The peroxide crosslinking reactions could increase the production of branches and, thus, the crystallization of branches and the extent of the endotherm shoulder.
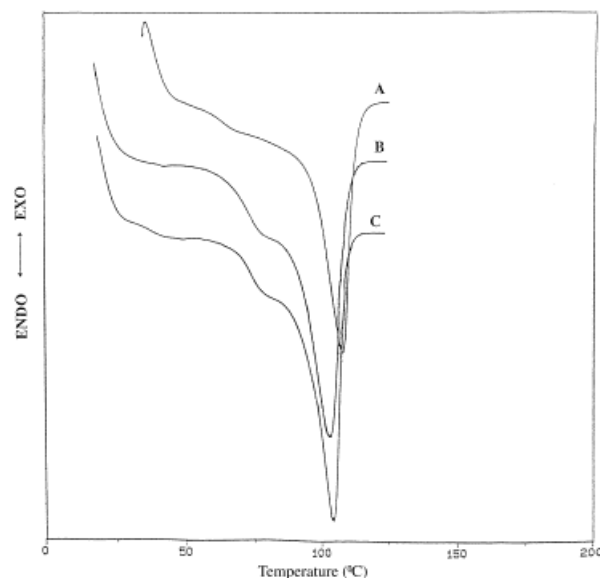
therm shoulder (Fig. 6), instead of an endotherm peak, was observed at 85°C for crosslinked sample AB1Cn. T_{m2} of sample AB1Cn was relatively low at about 104°C compared to those of AB2Cn and AB3Cn. The endotherm shoulder was due to the crystallization of branches of LDPE molecules. The cause of the different melting behavior for AB1Cn may be due to mixing of sol and gel fractions, or to the low extent of phase separation between sol and gel fractions. Compared to AB2 and AB3, AB1 was with the highest concentration of dicumyl peroxide at 0.15 phr. As suggested previously, the peroxide might induce crosslinking reactions during the silane grafting reactions when conducted in an extruder. Thus, the peroxide crosslinking reactions were perhaps sig-

Figure 6 DSC traces obtained from the first heating scan at a rate of 20°C/min under nitrogen for (A) LDPE, (B) AB1C2, and (C) AB1C4.

From TGA data, the decomposition temperatures of A1 and A1C2 were 467.8 and 479.8°C, respectively, both of which were much higher than that of LDPE at 425.7°C. The decomposition temperature of A1C2 was higher than that of A1 due to the effects of crosslinking reactions of the silane grafts with water. The crosslinks in A1C2 bound LDPE molecules together as a whole and retarded the chain scission of the LDPE molecules during TGA heating and, thus, led to an increase of decomposition temperature of A1C2. The crosslinking reaction time after 2 h was not a significant factor to the increase of decomposition temperature. The difference in decomposition temperatures between LDPE and A1 was 42.1°C and was significantly much higher than the difference (12.0°C) between A1 and A1C2. As previously demonstrated, the effects of the silane grafts on the decomposition temperatures were not observed. Thus, the peroxide-induced crosslinking reactions must have occurred during the peroxide-induced grafting reactions in the extruder and the crosslinking reactions were the main cause of the increase of decomposition temperature. The suggestion of the occurrence of the crosslinking reactions induced by dicumyl peroxide for A1 was consistent with the previous discussion.

CONCLUSIONS

Vinyl trimethoxysilane grafting reactions of LDPE were performed in an extruder, followed by crosslinking with boiled water. The thermal properties of both silane-grafted and silane-grafted water-crosslinked LDPE were investigated using DSC and TGA.

For Silane-Grafted LDPE

DSC data showed that the silane grafts on the LDPE molecules were thermal stable in the absence of moisture under 130°C, under which the silane-grafted LDPE could be processed or recycled. The silane grafts on the LDPE molecules reduced the melting point of LDPE and gave rise to an endotherm shoulder at about 85°C. TGA data showed that the decomposition temperature of the silane-grafted LDPE was much higher than that of LDPE. It was demonstrated that the cause

of the increase in the decomposition temperature was not due to the silane grafts but due to the peroxide-induced crosslinking reactions during the silane grafting reactions performed in an extruder.

For Silane-Grafted Water-Crosslinked LDPE

From DSC data, silane-grafted water-crosslinked LDPE displayed multiple melting behavior resulting from phase separation during crosslinking of LDPE with water. The phase separation gave rise to 2 melting points, including one at about 94°C, and the other at about 107°C. The latter was close to the melting point of LDPE and was due to the sol fraction of the material, while the former was due to the gel fraction of the material. The multiple melting behavior (or phase separation) disappeared during the second heating scan or beyond in the DSC measurements.

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