Silane-Crosslinked Ethylene–Octene Copolymer Blends: Thermal Aging and Crystallization Study

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ABSTRACT: Thermally stable materials can be achieved by crosslinking. This article presents the thermal aging and thermal energy storage properties of ethylene–octene copolymer (EOR) and low-density polyethylene (LDPE) blends as affected by silane crosslinking. Fourier transform infrared spectroscopy revealed a similar degree of silane grafting among the various blend compositions. However, the highest crosslink content was observed in EOR, whereas the lowest was found for LDPE. From melting temperature and heat of fusion data, a linear relationship between the amount of the crystalline component and the crosslink content was found. The decrease in crystallinity due to crosslinking was very limited, which implied a high thermal energy storage capacity of the silane-crosslinked products and their good mechanical properties at room temperature. Furthermore, a strong ability to retain the properties after thermal aging indicated good thermal stability of the materials. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2522–2528, 2008

Key words: ageing; blends; crosslinking; crystallization; structure

INTRODUCTION

Thermally stable materials are generally achieved by crosslinking. Crosslinked polymers, especially polyethylene (PE), have become commonly used for a number of industrial applications, including wire and cable coating, hot-water piping insulation, and heat-shrinkable products. Different procedures may be used for the initiation of crosslinking. One of them is based on the formation of silane-crosslinkable materials via the free-radical grafting of vinyl silane in the presence of peroxide. The silane-grafted polymer is then hydrolyzed and crosslinked in the solid state by the formation of siloxane (Si—O—Si) linkages. The chemistry of the reaction is shown in Figure 1. Because of the technological importance, a number of research studies have been carried out on this topic.[1–17]

Substantial changes in the polymer structure and properties can occur during the crosslinking process. However, extensive studies on this area are few, and the understanding of how the siloxane-crosslinked network affects the crystallization and thermal properties of a polymer remains matters of controversy. Transmission electron microscopy studies of silane-grafted PE, including high-density PE, linear low-density polyethylene (LLDPE), and low-density polyethylene (LDPE),

were carried out by Wong and Varrall.[1] Their results reveal dramatic changes in the lamellar distribution and length of the silane-grafted polymers. The molecular structure change varied according to PE type.[1] The studies of Celina and George[2] showed that silane crosslinking did not affect the properties of LDPE in the same manner as did peroxide crosslinking. The melting temperature (T_m) and enthalpy of silane-crosslinked polymers remained nearly constant, whereas a drastic decrease in T_m and enthalpy was observed in the peroxide-crosslinked samples. This result seemed to be in contrast with the findings of Shieh and Hsiao,[3] who reported multiple melting behavior of silane-crosslinked LDPE. Two melting points were observed at about 107.0 and 94.0°C and were reported to be due to two crystalline structures, including sol (107.0°C) and gel (94.0°C) fractions in the crosslinked material. As the crosslinking time increased, the melting point of the gel fraction decreased, whereas the melting point of the sol fraction increased. In their study, peroxide-induced crosslinking also occurred simultaneously during the grafting reactions. This complicates the assessment of crystallization occurring in silane-crosslinked material. Kuan et al.[4] reported an improvement in the mechanical properties of LLDPE after silane–water crosslinking. However, the increase in the mechanical properties observed was found to be mainly due to the self-crosslinking of LLDPE during the silane-grafting process.[4]

In this study, the characteristics of silane-crosslinked ethylene–octene copolymer (EOR) and LDPE blends were investigated. The LDPE was incorporated into the system to improve the blend stiffness and thermal properties. The silane-grafted samples were prepared
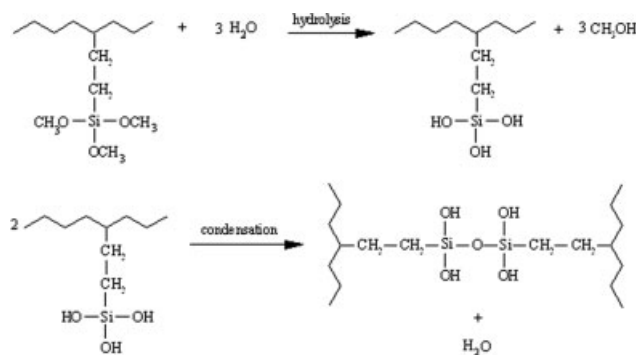
Figure 1 Silane-water crosslinking reaction.

by the melt-grafting of 5% vinyl trimethoxysilane in the presence of 0.1% dicumyl peroxide in a twin-screw extruder under conditions where the self-cross-linking reaction due to the presence of peroxide could be avoided. The grafted products were then analyzed with Fourier transform infrared (FTIR) analysis. The polymers were crosslinked in hot water in the absence of a catalyst. With this method, the progress in the crosslinking reaction could be monitored, and the influence of the formed crosslinking network on the crystallization, tensile properties, thermal aging, and thermal energy storage ability of the polymers could be solely determined.

EXPERIMENTAL

Materials

EOR (Engage E8003) with a melt flow index of 1.0 g/10 min was purchased from DuPont Dow Elastomer Co., Ltd. (Wilmington, DE). LDPE (LD2022) with a melt flow index of 0.25 g/10 min was supplied by Thai Petrochemical Industry Public Co., Ltd. (Bangkok, Thailand). The peroxide and silane used were dicumyl peroxide and vinyl trimethoxysilane, respectively. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used without purification.

Sample preparation

Preparation of the polymer blend

Various blends were prepared by the melt-mixing of EOR and LDPE in an intermeshing corotating twin-screw extruder (PRISM TSE 16, Staffordshire, United Kingdom). The barrel temperatures were set in the range 160–200°C. The screw speed was kept constant at 170 rpm. The concentrations of LDPE in the blends were varied as 0, 10, 30, 50, and 100 wt %.

Preparation of the silane–water-crosslinked polymer

The silane grafting reactions of the EOR blends were carried out in the molten state with a corotating twin-screw extruder (PRISM TSE16). The diameter of the screw was 16 mm, and the ratio of length to diameter was 25. The extruder was operated at a speed of 30 rpm with a sequence of segment temperatures at 160, 200, 170, 170, and 170°C from feed zone to die zone. The total reaction was finished within 5 min. Under these particular conditions, the barrel temperature next to the feed zone was set at 200°C to facilitate the thermal decomposition of the peroxide initiator. In the following zones, a flat temperature of 170°C was used across the extrusion barrel to minimize the extensive degradation and self-crosslinking of EOR in the extruder. These conditions were proven to yield a high grafting efficiency without peroxide-induced crosslinking as a side reaction.[5,6] To conduct a silane–water crosslinking reaction, the grafted samples were immersed in hot water at 70°C for a specified time. In this study, no catalyst was used to accelerate the crosslinking reaction.

Characterization

#### FTIR analysis of the silane-grafted polymer

FTIR spectroscopy was used to analyze the presence of silane in the grafted products. Films (50 μm thick) were prepared by hot-pressing at 190°C. Before the FTIR measurements, the films were washed with an excess volume of acetone to remove unreacted silane and residual peroxide. The IR spectra were then recorded with a PerkinElmer system 2000 FTIR spectrometer (Boston, MA) in the range 600–4000 cm^{-1} with a resolution of 4 cm^{-1}.

Gel content analysis

The content of gel or insoluble fraction of water-crosslinked material after solvent extraction was determined according to ASTM D 2765-01. A sample of about 0.3 g was wrapped in a 120-mesh stainless steel cage and extracted in refluxing xylene containing 1% antioxidant [Irganox 1010, Ciba-Geigy (Basle, Switzerland)] for 6 h. After extraction, the samples were weighed after they were dried in a vacuum oven until a constant weight was reached. The gel content was calculated with the following equation:

$$\text{Gel content } (\%) = \frac{\text{Final weight of sample}}{\text{Initial weight of sample}} \times 100$$

All grafted samples that had not been water-cross-linked contained no gel.
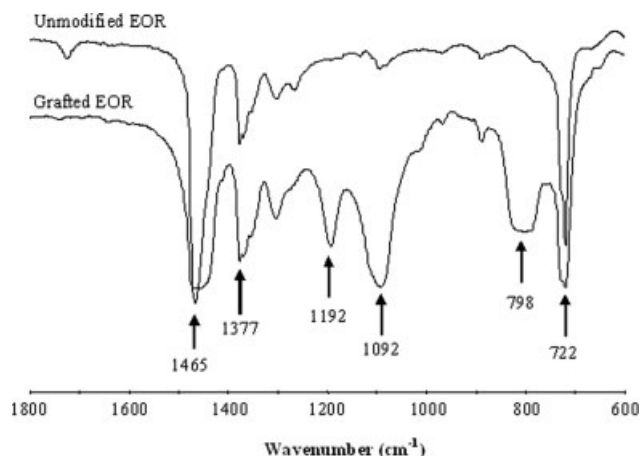
Figure 2 FTIR spectra of the unmodified EOR and silane-grafted EOR.

Differential scanning calorimetry (DSC)

To study the effect of crosslinking on the crystallization and structure of EOR blends, the thermal behaviors of the samples before and after crosslinking were analyzed with a PerkinElmer DSC-7. The test specimens (5 ± 1 mg) were heated from 50 to 150°C at a scanning rate of 20°C/min. The temperature was then maintained at 150°C for 5 min before it was cooled to 50°C at the same rate.

Thermogravimetric analysis (TGA)

A PerkinElmer TGA-7 thermogravimetric analyzer was used for the thermal decomposition investigation. The apparatus was continually flushed with nitrogen gas. A sample (5 ± 1 mg) was placed in a platinum sample pan and then heated to 600°C at a rate of 20°C/min. The weight percentages of the samples were measured as a function of temperature.

Thermal aging test

Dumbbell specimens 1 mm thick were stamp-cut from a compression-molded sheet and then crosslinked in hot water at 70°C for 120 h. The crosslinked speci-

mens were then hung in a hot-air oven at 110°C for 12 h before their tensile properties were measured. The tensile test was carried out with an Instron tensile tester [model 5569 (Norwood, MA)] with a crosshead speed of 500 mm/min and a 1-kN load cell.

RESULTS AND DISCUSSION

Silane-grafted EOR/LDPE blends

Figure 2 shows the FTIR spectra of the unmodified EOR and silane-grafted EOR samples. The characteristic peaks of EOR at 1377 and 1465 cm^{-1} corresponded to the C—H bending vibrations of the methyl and methylene groups of EOR, respectively. After the grafting reaction, three additional peaks corresponding to the trimethoxysilane (Si—OCH$_3$) groups of the grafted samples were seen at 798, 1092, and 1192 cm^{-1}. The grafting indices in various samples were determined by calculation of the ratio of absorbance of the 1092-cm^{-1} band, corresponding to the Si—OCH$_3$ group in the grafted polymer, to the absorbance of the methyl group band at 1377 cm^{-1}, which was used as the internal reference in the normalization of the different spectra. The reported values were obtained, with at least five measurements in different points of the samples averaged. The calculated grafting degrees of EOR, LDPE, and their blends, as demonstrated in Table I, showed only slight differences among these samples. With the energy required for bond breaking considered, the homolytic bond dissociation energies for hydrogen attached to the primary, secondary, and tertiary carbons were 410, 397, and 385 kJ/mol, respectively.[18] Thus, the lowest energy needed for a free radical to abstract hydrogen was from a tertiary carbon among the three kinds of carbons. Compared the two polymers used, LDPE had a long branch structure with the number of branches in the range 20–30 methyl groups per 1000 carbons.[18] In the case of EOR, which was one of the LLDPE groups, it usually had a number of short-chain branchings in the range 20–50 methyl groups per 1000 carbons.[19] For LLDPE with a similar octene content to that in the

TABLE I
T_m, ΔH_f, T_c, and $T_{c\ onset}$ Values of the Unmodified and Various Grafted EOR/LDPE Blends

System	LDPE (%)	Grafting index	T_m (°C)	ΔH_f (J/g)	T_c (°C)	$T_{c\ onset}$ (°C)
Unmodified blends	0	—	60–100	23.8	56.1	60.4
	10	—	65–115	23.5	70.2	74.1
	30	—	108.1	39.1	80.8	93.7
	50	—	110.0	57.5	88.8	95.0
	100	—	111.1	90.6	93.7	97.7
Grafted blends	0	2.87	60–100	19.6	58.7	63.8
	10	2.71	65–115	21.5	66.4	74.8
	30	2.94	105.6	36.5	79.1	91.9
	50	3.23	108.7	48.7	86.3	94.6
	100	2.81	111.1	81.8	92.7	97.7
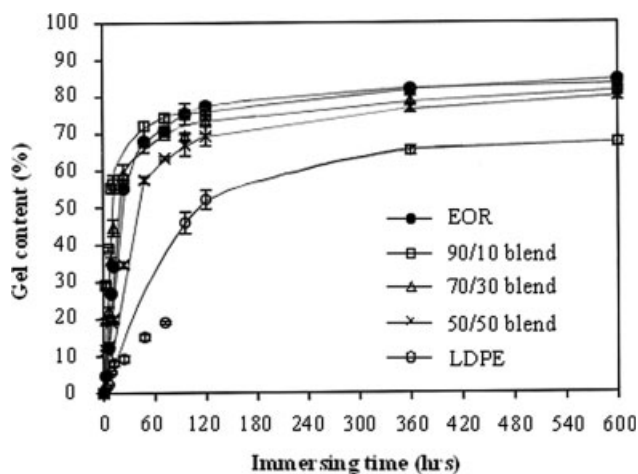
Figure 3 Gel content as a function of immersion time for the EOR/LDPE blends.

EOR used in this study (7%mol), Parent et al.[20] reported a structure with 31 tertiary carbons per 1000 carbons. Because of a similar structure between the two polymers used in this study and the small amount of silane (5%) used in the reaction, only a slight difference in grafting degree was found among the various blend compositions.

## Crosslinking of silane-grafted EOR/LDPE blends

After conducting a crosslinking reaction in water, we determined the contents of gel in the various EOR/LDPE blend samples as a function of immersing time. As expected, the content of gel increased with increasing crosslinking time (Fig. 3). All samples showed a similar trend but with different magnitudes of gel content obtained. Although they had similar grafting degrees, the EOR yielded a higher gel content of 85%, whereas the LDPE showed only 67% gel after 600 h of crosslinking. In the blend systems, the maximum contents of gel decreased with increasing LDPE concentration, that is, 83, 81, and 80% gel in the case of the 90/10, 70/30, and 50/50 blends, respectively. In this study, a linear relationship was observed between the crosslink content and amount of crystalline component in the blends, as shown in Figure 4. Not only the crosslinking degree but also the rate of crosslinking varied among the blend samples. For a particular blend, the crosslinking rate was comparatively high in the early stage of the crosslinking process and slowed down thereafter. By analyzing the slope in the initial stage of the graph, we estimated the crosslinking rate. The rate of crosslinking of EOR was approximately six times higher than that of LDPE. The substitution of EOR by LDPE in the blend, therefore, caused some changes in the crosslinking rate. As the content of LDPE in the blends increased, the rate of crosslinking decreased systematically. The reason for this is

believed to a lower rate of water diffusion in LDPE during the crosslinking reaction, brought about by its higher crystalline portion.

Melting and crystallization behaviors

The melting and crystallization behaviors of the EOR/LDPE blends are illustrated in Figure 5. The DSC results are summarized in Table I. The unmodified EOR showed a broad melting thermogram ranging from 60 to 100°C. The broad endotherm observed in this sample is believed to be due to the distribution in the length of crystallizable ethylene sequence imposed by the placement of noncrystallizable comonomer units along the chains, with the consequence of a broad distribution of crystal sizes in this polymer. In contrast to EOR, LDPE showed a sharp melting peak with a T_m of 111°C. In the EOR/LDPE (90/10) blend, a wide melting endotherm ranging from 60 to 115°C was observed. This may have been due to a variation in crystal sizes in the system. When further increases in the LDPE concentration, the T_m peaks of the blends increased and shifted toward the T_m of LDPE. Not only the T_m but also the values of the enthalpy of fusion of the sample (ΔH_f), crystallization temperature (T_c), and crystallization temperature onset ($T_{c\ onset}$) increased systematically with increasing LDPE concentration in the blends. The grafted silane showed only a slight effect on the melting and crystallization behaviors of the blends, as shown in Table I.

Figure 6(a) shows the DSC heating thermograms of the EOR samples before and after a crosslinking reaction was conducted. It was interesting to see the sharp melting endotherm of the crosslinked EOR sample showing a T_m peak at 87°C, which was unlike to that observed for the unmodified EOR sample. These results infer that recrystallization of some chain segments may have occurred during the
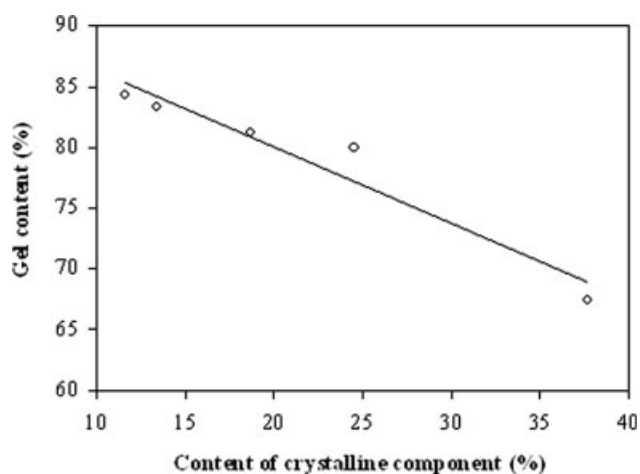
Figure 4 Relationship between the gel content and crystallinity in various crosslinked blends.
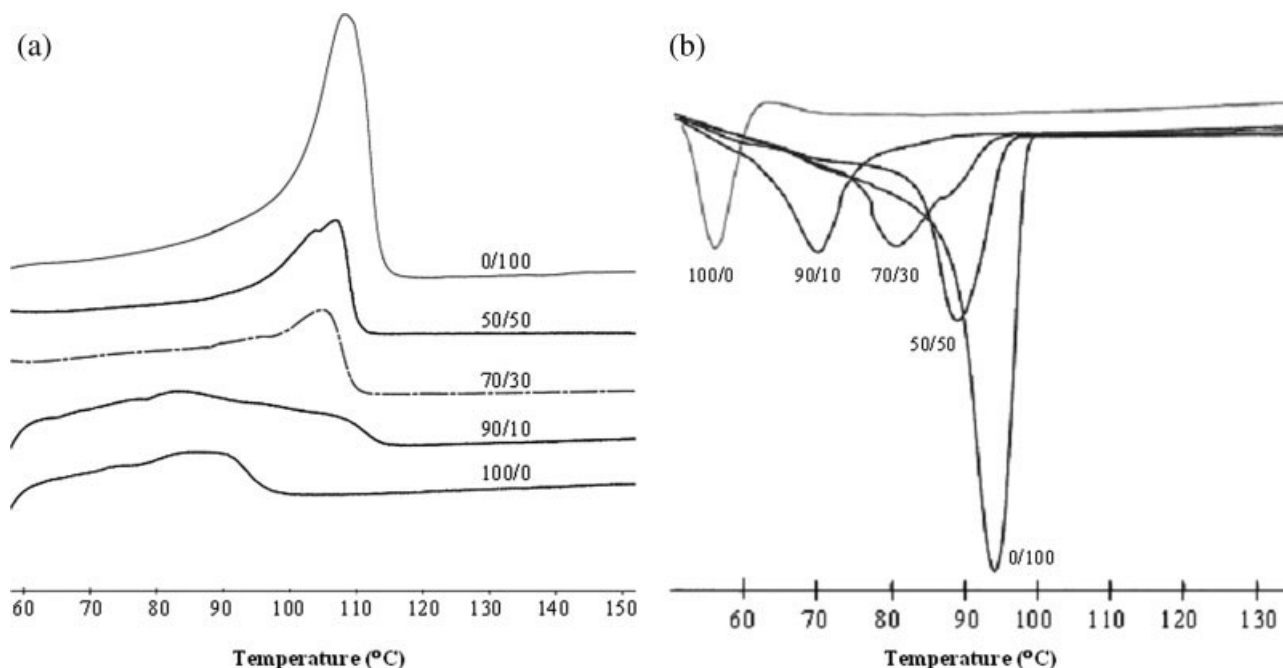
Figure 5 DSC (a) heating and (b) cooling thermograms of various EOR/LDPE blends.

crosslinking reaction and led to some changes in the polymer microstructure. To verify whether the conditions used in the crosslinking process induced changes in crystal structure of the silane-grafted polymers and how the crosslinking and crystallization processes interfered with each other, some selected samples were annealed under the same testing conditions as used in the crosslinking process. DSC analyses on the annealed samples were then carried out. An endotherm that was similar to that observed for the crosslinked product was clearly seen in the annealed sample. During a long crosslinking time, any chain segments that were long enough to crystallize had sufficient time for the recrystallization process and formed into a more well-defined crystal structure. This finding was also observed in the blend systems. Clearly, the split of the T_m peaks of EOR and LDPE was observed in the DSC thermograms of the 70/30 and 50/50 blends. An example of a DSC thermogram of the crosslinked 70/30 blend is shown in Figure 6(b). The crosslinked samples and annealed samples of all of the blend series showed only slight differences in the T_m, T_c, T_c onset, and ΔH_f values (Table II). This suggested an important point: that silane crosslinking did not disturb the recrystallization process of the blends. Silane crosslinking was, therefore, believed to have preferentially taken place in the amorphous region.

Thermal stability and energy storage capacity

An investigation of the thermal stability of the crosslinked products was performed with TGA. The decomposition temperatures (T_d's) of all of the blends before and after crosslinking are shown in Table II. T_d of EOR was observed at 473°C, whereas LDPE showed a T_d at 490°C. With the incorporation of LDPE into the system, the T_d's of the blends shifted slightly to higher temperatures. The thermal degradation was undergone and was completed around 550°C, with no residue at the end of the degradation. The presence of silane crosslinking increased the T_d's of the blends to some extent, in particular those with higher concentrations of EOR. An insignificant increase in T_d is found for the LDPE system. This could have been due to a lower degree of crosslinking in this system, as compared to that in EOR. Correlations between the thermal stability and crosslink density have been studied with contradictory results in the literature.[21–23] For a peroxide-crosslinked system, Krupta and Luyt[21] reported a similar T_d for LLDPE/wax blends containing different crosslink densities. Zong et al.[22] found that silane-crosslinked LLDPE samples were more stable than uncrosslinked LLDPE. The thermal stability of the crosslinked polymer was enhanced with increasing gel content. By contrast, Khonakdar et al.[23] reported that the thermal stability of high-density PE was independent of crosslinking.

Thermally stable materials are generally achieved by crosslinking. These materials do not undergo melt flow, even when they are heated above the crystalline T_m. However, one of the drawbacks of crosslinking is a reduction in the polymer crystallinity and heat of fusion.[7,13] In some applications, such as insulation for a heat-exchanger unit, a material
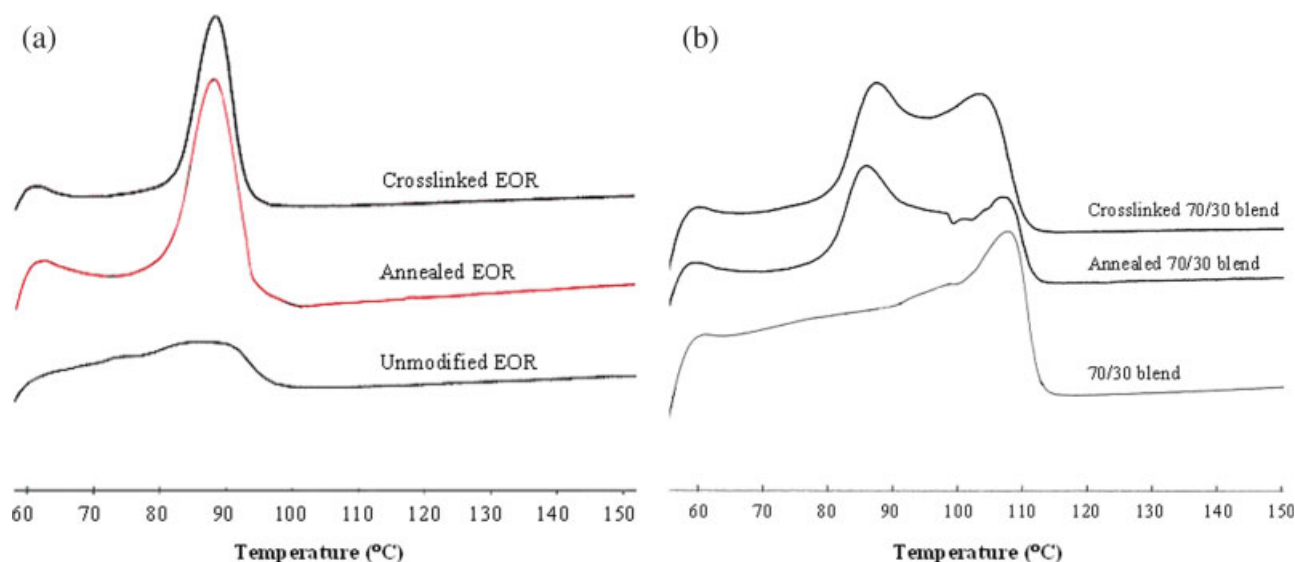
Figure 6 DSC heating thermograms of (a) unmodified EOR, annealed EOR, and crosslinked EOR samples and (b) the EOR/LDPE (70/30) blend, its annealed sample, and crosslinked sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with a high thermal energy storage capacity is needed. To investigate the effect of crosslinking on the energy storage ability of a polymer, the retention of ΔH_f (or % ΔH_f retained) of the polymer after the crosslinking reaction is determined with the following equation:

$$\%\Delta H_f \text{ retained} = \frac{\Delta H_f \text{ of the crosslinked sample}}{\Delta H_f \text{ of the pure polymer}} \times 100$$

(2)

The pure polymer used is subjected to the same conditions as the crosslinked samples.

For peroxide-crosslinked polymers, a significant drop in ΔH_f[8,23–25] and % ΔH_f retained was reported.[8,26] This was due to the fact that peroxide crosslinking was performed above the T_m of the polymer crystallites. Crosslinks play the role of

defect centers, which impede the folding of polymer chains and result in a decrease in the sizes of the lamellar crystals.[25] In this study, silane crosslinking caused a very slight disturbance in the crystallization of the LDPE and 50/50 blend samples; values of % ΔH_f retained of 92 and 95%, respectively, were observed in these samples. In the case of crosslinked EOR and the 90/10 and 70/30 blends, no loss in crystallinity due to crosslinking was observed. Those samples showed 100% ΔH_f retained. Therefore, it could be said that all silane-crosslinked samples investigated in this study had a strong potential to be used for thermal energy storage applications.

Thermal aging properties

In this study, the tensile behaviors of all of the silane-crosslinked blends before and after an aging test

TABLE II
T_m, ΔH_f, T_c, $T_{c \text{ onset}}$, T_d, and % ΔH_f Retained of the Crosslinked and Annealed EOR/LDPE Blends After Crosslinking for 120 h

System	LDPE (%)	Gel (%)	T_{m1}, T_{m2} (°C)	ΔH_f (J/g)	T_c (°C)	$T_{c \text{ onset}}$ (°C)	T_d (°C)	% ΔH_f retained
Crosslinked blends	0	77	87.0	33.1	58.5	63.4	491	100
	10	75	88.0	37.9	66.9	74.5	484	100
	30	74	87.1, 103.6	51.5	79.3	92.1	483	100
	50	69	87.2, 105.4	70.8	86.8	95.2	486	95
	100	52	109.1	99.6	93.0	98.2	491	92
Annealed blends	0	—	86.7	31.8	56.2	60.3	473	NA
	10	—	86.1	34.9	69.7	77.4	477	NA
	30	—	85.6, 106.7	50.1	78.7	89.8	479	NA
	50	—	88.8, 110.0	74.3	88.3	94.8	492	NA
	100	—	110.3	107.8	94.1	97.6	490	NA

NA = not applicable.
T_{m1} = melting temperature of EOR.
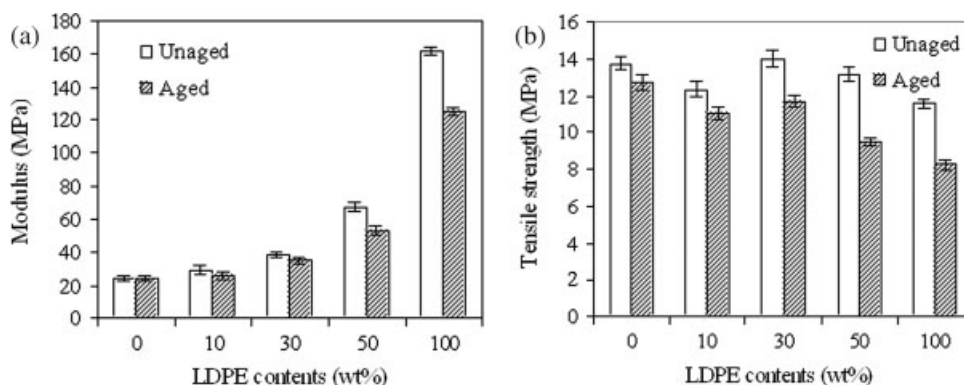T_{m2} = melting temperature of LDPE.

Figure 7 (a) Modulus and (b) tensile strength of the crosslinked blends before and after the thermal aging test.

at 110°C were characterized. Under this aging experiment, all of the uncrosslinked blends failed to withstand the heat. This was expected because the aging temperature used was higher than the T_m of the EOR/LDPE blends. The uncrosslinked samples deformed and flowed upon heating in a hot-air oven for a short period of time. Apparently, only the crosslinked materials could withstand such a high-temperature environment. Figure 7 shows the tensile properties after the thermal aging experiment. Reductions in tensile modulus and strength were observed after thermal aging. Such reduction were more obvious in LDPE than in EOR, even though the aging temperature used in the study (110°C) was 20° higher than the T_m of EOR (87°C). The silane-crosslinked blends with higher EOR concentrations exhibited better abilities to retain their properties after the aging test than those with lower EOR concentrations. This indicates that the degree of crosslinking played a significant role in controlling the high-temperature properties of the polymers.

CONCLUSIONS

Various silane–water crosslinked EOR/LDPE blends were prepared under conditions where the self-crosslinking of EOR and LDPE induced by peroxide during reactive extrusion could be negligible. The crosslinked products were characterized for their thermal properties with several techniques, including FTIR, DSC, TGA, and tensile and aging tests. The degree of crosslinking, as determined by the content of gel, increased with increasing crosslinking time. The crosslinking degree and rate were found to depend strongly on the amount of crystalline and amorphous portions in the blends. DSC results revealed that the recrystallization of some chains occurred simultaneously during the crosslinking reaction. The silane-crosslinked products exhibited good thermal stability and energy storage ability. Af-

ter the aging test, all uncrosslinked materials failed to withstand the aging heat. This was unlike the crosslinked samples. The extent of crosslinking was found to play a major role in the high-temperature properties of the polymers.

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