Comparison in Processability and Mechanical and Thermal Properties of Ethylene–Octene Copolymer Crosslinked by Different Techniques

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ABSTRACT: The crosslinking of metallocene ethylene–octene copolymer was investigated. The crosslinked polymers were prepared using two different techniques, i.e., peroxide crosslinking and silane–water crosslinking. In the former, the crosslinking reaction was conducted in a twin-screw extruder, in the presence of dicumylperoxide. In the latter, the polymer was first grafted with vinyl trimethoxysilane in the extruder and subsequently crosslinked with water. The paper aims at investigation of the differences between these two techniques, in terms of processing and product mechanical and thermal properties. The results showed that the silane-crosslinked polymers could be pre- pared with much higher gel contents than the peroxide-crosslinked samples. The silane-crosslinked polymers also retained the elastomeric characteristics of the pure polymer and showed remarkably higher extensibility, better thermal stability, and energy storage capacity. An explanation for the property differences between peroxide-crosslinked and silane-crosslinked polymers was proposed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1179–1185, 2004

Key words: peroxide; silane-grafting; ethylene–octene copolymer; crosslinking

INTRODUCTION

Crosslinking is an important method for improving polymer properties, in particular, high-temperature properties. There are several effective methods of crosslinking polymer, including irradiation crosslinking,[1–4] peroxide crosslinking,[5–11] and silane–moisture crosslinking.[12–19] In the present study, peroxide crosslinking and silane–moisture crosslinking are of interest. In the case of peroxide crosslinking, peroxide is used as a heat-activated chemical that generates free radicals for crosslinking. Peroxides undergo thermal decomposition into oxy radicals, which abstract a hydrogen atom from the polymer to generate polymer radicals. These radicals then react to form carbon–carbon (C–C) crosslinks. For silane–moisture crosslinking, the method involves grafting vinylsilane to the polymer backbone. The preferred silanes are unsaturated alkoxy silanes, such as vinyl trimethoxysilane (VTMS) and vinyl triethoxysilane (VTES). The crosslinking of silane-grafted polymer occurs through hydrolyzation of the hydrolyzable alkoxy groups with moisture, followed by condensation of the formed hydroxyl groups to form stable siloxane linkages (Si–O–Si).

Most published work related to this field is concerned with low density polyethylene (LDPE). Isac et al.[9] studied the peroxide crosslinking of LDPE and its blend systems in a single-screw extruder. They found that the amount of crosslinking increased with an increase of peroxide concentration.[9] Although this radical initiated modification is relatively simple, it has some processing limitations. The extrusion torque was reported to increase with increasing dicumyl peroxide (DCP) content and reached a maximum at 1% DCP.[9] An increase in torque level and die pressure was also observed by Lachtermacher et al.[5] in the case of linear low density polyethylene (LLDPEs) in a twin-screw extruder using 2,5-dimethyl-2,5-di (*t*-butylperoxy) hexane as an initiator. Apart from extrusion problems, peroxide crosslinked samples also showed difficulties in flowing into mold cavities in the shaping of products due to their high viscosity.

The silane–moisture crosslinking process, in contrast, is conducted after shaping the silane grafted polymer into final products. Therefore, products of good quality may be produced at relatively higher rates. The degree and rate of silane crosslinking were found to depend on crosslinking temperature and time[17] as well as thickness of sample.[12] To minimize the crosslinking time, the crosslinking reaction is accelerated with suitable catalysts such as di-*n*-butyltindilaurate, dibutyltin diacetate, and dibutyltin dioctoate.[17,18] The use of catalyst, however, leads to a

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problem involving the storage of the grafted product. The premature crosslinking of grafted product may occur easily.[17]

In the present study, the crosslinking of metallocene ethylene–octene copolymer (EOR) is investigated since the copolymer is a highly curable material and exhibits the flexibility inherent in its elastomeric nature. The crosslinked EORs were prepared using two techniques, i.e., peroxide crosslinking and silane–water crosslinking. A comparison between crosslinked polymers obtained from the two techniques was conducted. An attempt has been made to explain the differences in processing and product mechanical and thermal properties.

EXPERIMENTAL

Materials

Ethylene–octene copolymer grade ENGAGE E8003, DuPont Dow Elastomer Co. Ltd., was used. It contains 7.6 mol % of octene, with a molecular weight of 151.139 and density of 0.885 (g/cm^3). The peroxide used was DCP, supplied by Aldrich Chemical Co. The silane used was VTMS.

Preparation of crosslinked EOR

For peroxide-crosslinked EOR, the crosslinking reaction was carried out in a Prism TSE 16 intermeshing corotating twin-screw extruder, with a screw diameter of 16 mm and an effective length of 400 mm. The screws of the extruder were assembled from individual screw elements, including regular helical-shaped screw bushings, kneading blocks, and mixing elements for providing good conveying and mixing in the extruder. Dicumyl peroxide was initially dissolved in acetone and then coated on the EOR pellets. The concentrations of DCP were in the range of 0–0.5 % wt. A screw speed of 30 rpm and a temperature profile of 100, 130, 150, 190, and 190°C from feed zone to die zone were used. The total reaction was finished within 5 min. The half-life of DCP in molten state (~ 190°C) is less than 1 min.[20] The extrudate was cooled in a water bath and pelletized. The crosslinked products were then shaped into 1-mm-thick compression-molded sheets. This was done by preheating the polymers at 200°C for 5 min and then pressing at 15 MPa for 5 min. After cooling, a sheet was cut into tensile bars.

In silane-grafting process, the EOR pellets were premixed with VTMS and DCP. The mixture was kept immediately under N$_2$ gas in a sealed container. The polymer was then tumbled-mixed for 20 min and allowed to stand overnight. The concentrations of silane used were varied from 0 to 5 phr (part of reagent per hundred parts of EOR), while the concentration of

peroxide was kept constant at 0.1 phr. A screw speed of 30 rpm and a temperature profile of 160, 200, 200, 200, and 200°C from feed zone to die zone were used. The grafted products were then shaped into 1-mm-thick compression-molded sheets and cut into tensile specimens.

To conduct a crosslinking reaction, the samples were immersed in hot water (70°C) for a certain time. This temperature was below the melting temperature of E8003 (T_m ~ 78°C). In this study, no catalyst was used for accelerating the crosslinking reaction to avoid problems involving premature crosslinking during storage of grafted product. From the work of Narkis et al.,[17] crosslinking of grafted high density polyethylene (HDPE) containing 5% of catalyst was reported to occur during storage in a desiccator at 23°C. The gel content of 20% was obtained after only 25 h of crosslinking time.

Characterization and testing

FTIR analysis of silane-grafted EOR

Fourier-transform infrared spectroscopy was used to analyze the presence of silane in the grafted products. Films (50 μm thick) were prepared by hot pressing at 200°C. Prior to FTIR measurement, the films were washed with an excess volume of acetone for 1 min to remove unreacted silane or residual peroxide. It was found that the grafting index (the extent of silane grafting) obtained from this procedure was not different from that from extraction by refluxing with acetone for 10 h.[21] The IR spectra were then recorded using a Perkin–Elmer system 2000 FTIR spectrometer in the range of 600–4,000 cm^{-1} with a resolution of 4 cm^{-1}.

Gel content

The gel content or insoluble fraction of crosslinked EOR was determined according to ASTM D2765-95a by mass of polymer insoluble after extraction. The sample of about 0.3 g was wrapped in a 120-mesh stainless-steel cage and extracted in refluxing xylene containing 1% of antioxidant (Irganox 1010, Ciba-Geigy) for 6 h. After extraction, the cage was dried in a vacuum oven at 55°C till constant weight was achieved. The gel content was calculated using the following equation.

$$\% \, \text{gel content} = \frac{\text{final weight of sample}}{\text{initial weight of sample}} \times 100 \quad (1)$$

Melt flow index

The melt flow index was determined using a Kayaness D-7053 instrument. The samples were melted at 230°C

and then driven through the capillary die using a 20.16-kg load. Weight of extrudate in grams unit at 10-min intervals was measured as the melt flow index (MFI).

Tensile testing

An Instron tensile tester (Model 4301) was operated at a crosshead speed of 500 mm/min using 1 kN load cell. The specimens were stamped cut from a 1-mm-thick compression-molded sheet. The dimension of test specimens used was type IV according to ASTM D 638–99. Tensile strength was determined from stress at rupture of specimen while the moduli at 100, 300, and 500% strain (M100, M300, and M500) were evaluated from tensile stress at 100, 300, and 500% elongation, respectively.

Differential scanning calorimetry

To study the thermal behaviors of crosslinked samples, a Perkin–Elmer DSC-7 was used. The samples ($\sim$ 5 mg) were heated from 10 to 150°C at a scan rate of 20°C/min. The temperature was then maintained at 150°C for 5 min before cooling to 10°C at the same rate. The melting and crystallisation behaviors of the samples before and after crosslinking were examined. The enthalpy of fusion of 290 J/g for 100% crystalline PE was used in the calculation of percent crystallinity.[22]

Thermal stability

The thermal stability of crosslinked products upon heating in an air oven was investigated. The samples were heated at 90 and 200°C. Any changes in sample shape, dimension, or appearance were detected.
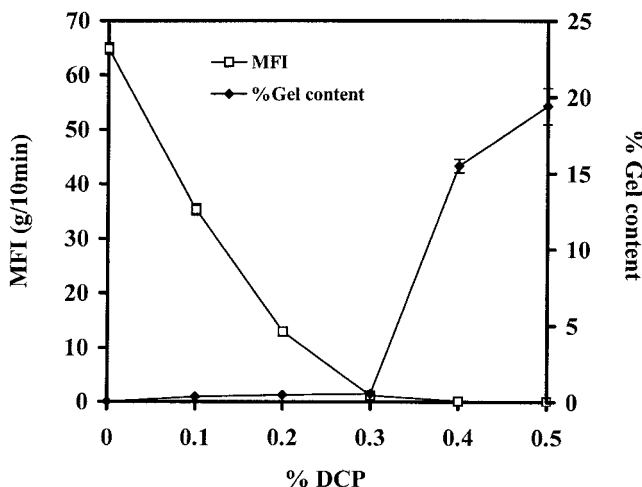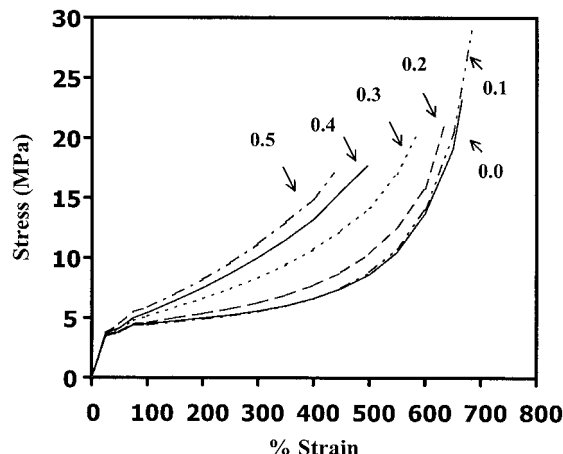

Figure 2 Stress–strain curves of peroxide-crosslinked samples. The peroxide concentrations were varied from 0 to 0.5%.

RESULTS AND DISCUSSION

Peroxide crosslinked EOR

Gel content

Figure 1 shows the evolution of gel and MFI for EOR crosslinked with different amounts of DCP. No gel is formed at low levels of peroxide. A transition point of gel increment is clearly seen at 0.3% DCP. Beyond this point, the gel content increases rapidly with increasing peroxide concentration. This is as expected since the higher the level of peroxide used, the higher the concentration of polymer radicals generated. It was reported previously that a peroxide concentration of at least 0.2% (w/w) should be used in the industrial crosslinking of polyethylene.[23,24]

The results of the gel are in accordance with those of MFI. The MFI values decrease systematically with an increase of peroxide concentration. At low levels of peroxide, although no gel is observed, a decrease in the MFI values is clearly seen. From the work of Lachtermacher and Rudin,[25,26] the effect of peroxide treatment on the molecular structure of LLDPE was studied. Peroxide levels were kept very low to avoid crosslinking. The results of gel content analysis indicated that the products were gel-free, but the ^{13}C-NMR spectra gave contrary indications where line-broadening in spectra was observed, suggesting that some crosslinking did occur. In this study, the use of peroxide lower than 0.2% might cause some crosslinking but the measurable amount of insoluble material after solvent extraction is not evident. The maximum gel content obtained from this technique is only 20%. During peroxide crosslinking reaction in a twin-screw extruder, the process torque and die pressure were so high that the extruder could not be properly operated. The DCP concentration used in this study was, therefore, limited to 0.5%.

Figure 1 Effect of DCP concentration on the gel content and MFI of peroxide-crosslinked EOR.

TABLE I
Tensile Results of Peroxide Crosslinked Samples

DCP (%)	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)
0	23.19 (1.12)[a]	666.10 (13.94)	4.46 (0.04)	5.56 (0.07)	8.62 (0.17)
0.1	28.94 (2.17)	683.34 (16.28)	4.38 (0.09)	5.50 (0.13)	8.79 (0.38)
0.2	21.30 (2.09)	636.22 (24.37)	4.58 (0.15)	6.26 (0.39)	10.33 (0.64)
0.3	20.27 (0.41)	585.90 (15.01)	5.12 (0.36)	8.34 (0.75)	14.15 (0.77)
0.4	17.68 (0.92)	496.80 (23.10)	5.41 (0.18)	10.03 (0.56)	-
0.5	17.04 (1.02)	437.30 (32.77)	5.87 (0.41)	11.16 (1.00)	-

[a] Values in parentheses are standard deviations.

Tensile properties

Figure 2 shows the stress–strain curves of EOR before and after crosslinking. Pure EOR exhibits uniform deformation and stress-upswing at high strains, illustrating its elastomeric nature. In the presence of peroxide, crosslinking occurs, leading to significant changes in the stress–strain behaviors. These changes can be observed clearly at high strains ($> 500\%$ strain) and high crosslinking levels ($> 0.3\%$ DCP). This demonstrated that crosslinking has no role on the tensile behaviors at low strains ($< 50\%$ strain). The effect of the crosslink network on the tensile response is significant only at intermediate and high strains. As seen in Figure 2, with increasing peroxide content the strain hardening at high elongations was less pronounced. The tensile behaviors change from uniform deformation and stress upswing at high strains to low extensibility and fracture at lower strains. It was reported by Matsuoka and Kawai[27] that strain hardening in PE was caused by strain-induced crystallization and it was likely that this type of crystallization was hindered by the crosslinks.
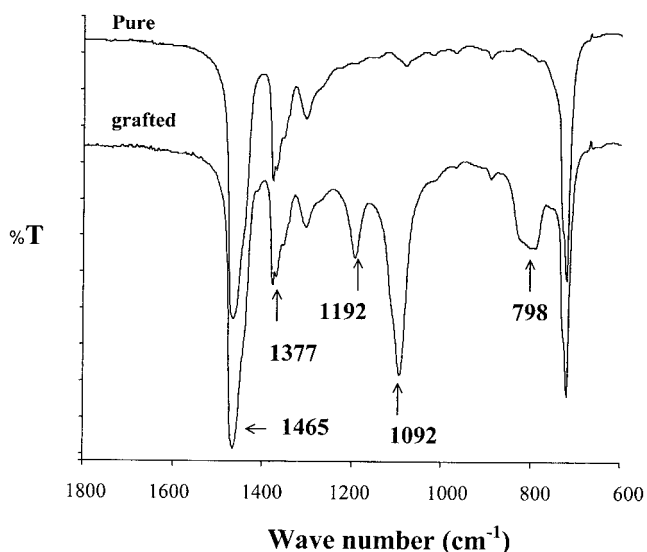
Table I shows the tensile results. It can be seen that an increase in DCP concentration, or in the other words, a higher degree of crosslinking leads to an increase in modulus but a decrease in elongation at break and tensile strength. This can be explained by the restriction of chain movement brought about by the crosslink network.

Silane–water crosslinked EOR

Gel content

In this study, the EOR samples were first grafted with VTMS via a free-radical reaction in a twin-screw extruder, under the appropriate conditions in which premature crosslinking during processing is avoided. Figure 3 shows the FTIR spectra of EOR samples before and after the grafting reaction. The characteristic peaks observed at 1,377 and 1,465 cm^{-1} correspond to the C–H stretching vibrations of the methyl and methylene groups, respectively. After the silane grafting reaction, three additional peaks corresponding to the trimethoxy silane group [Si–(O–CH$_3$)$_3$] in the sample were observed at 798, 1,092, and 1,192 cm^{-1}.

To conduct a crosslinking reaction, the grafted polymer was shaped into final products and subsequently
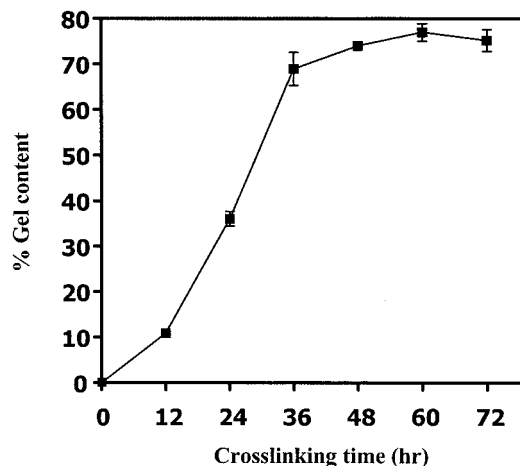

Figure 3 FTIR spectra of EOR before (a) and after (b) grafting with 5% VTMS.

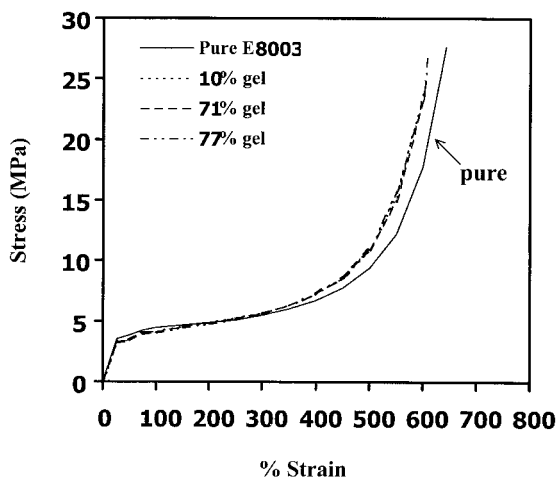**Figure 4** Effect of crosslinking time on the gel content.

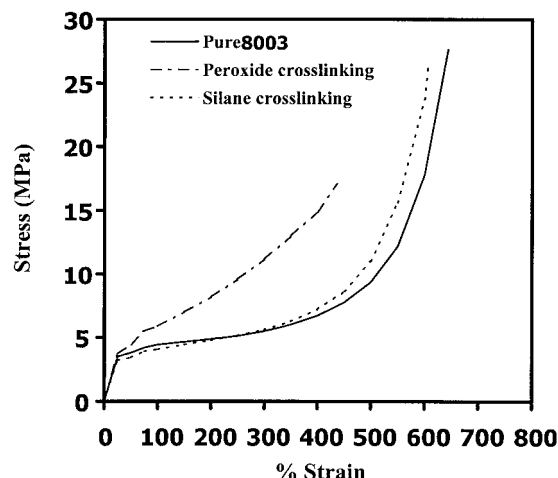**Figure 5** Stress–strain curves of silane–water crosslinked samples.

Figure 6 Stress–strain curves of pure EOR, peroxide-crosslinked EOR, and silane–water-crosslinked EOR

immersed into hot water at 70°C. The effect of immersion time on the gel content is investigated and the results are shown in Figure 4. The rate of gel formation as determined by the slope of the initial linear portion of lines is high in the early stage of crosslinking. Thereafter, the rate decreases and the maximum gel content of ~ 75–80% is reached after about 60 h of immersion time. The level of gel obtained from this study is the same as that used in industrial practice, e.g., when producing cable insulation, with ethylene vinyltrimethoxysilane copolymer.[19]

Tensile properties

Figure 5 shows the stress–strain curves of silane–water-crosslinked polymers. The tensile results are shown in Table II. Unlike peroxide-crosslinked EOR (Fig. 2 and Table I), the tensile properties of pure EOR and silane–water-crosslinked EOR are not much different. All silane–water-crosslinked samples show uniform deformation and stress-upswing at high strains. The differences in tensile properties among various samples are within standard deviations. Our tensile results are similar to those reported by Celina and George[28] in which no significant difference in mechanical properties was observed between pure LDPE and its silane-crosslinked sample.

Comparing the properties of crosslinked samples obtained from peroxide-crosslinking and silane–water-crosslinking techniques

Tensile properties

Figure 6 shows the stress–strain curves of uncrosslinked EOR and its crosslinked samples containing similar gel content of approximately 20%. After crosslinking, the silane-crosslinked sample retains the original characteristics of EOR. A uniform deformation and stress-upswing at high strains can be clearly seen. Significant change of tensile behavior is observed in the case of the peroxide-crosslinked sample, where low extensibility and fracture at lower strains are resulted. To explain this difference, we first have to realize that the peroxide-crosslinking reaction took place during extrusion where the polymer was in the molten state, whereas the silane–water-crosslinking reaction occurred when the polymer was in the solid state. Due to the limitation of polymer chain mobility in the latter case, some inhomogeneity may be present and produce a network with some highly crosslinked areas alternating with uncrosslinked regions. The chains in these uncrosslinked regions are able to deform and behave like those in pure polymer. It was reported previously that crosslinking of PE upon irradiation in the solid state preferentially took place in

TABLE II
Tensile Results of Silane–Water Crosslinked Samples

VTMS (%)	Gel content (%)	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)
Pure	Pure	27.64 (2.54)[a]	643.75 (10.30)	4.43 (0.08)	5.49 (0.11)	9.37 (0.40)
1	10.62	21.16 (1.47)	585.40 (7.36)	4.10 (0.05)	5.73 (0.04)	10.85 (0.13)
3	71.18	24.72 (4.30)	606.20 (17.11)	4.18 (0.12)	5.71 (0.13)	10.84 (0.17)
5	77.01	26.54 (4.00)	607.90 (26.05)	4.05 (0.11)	5.60 (0.13)	11.00 (0.53)

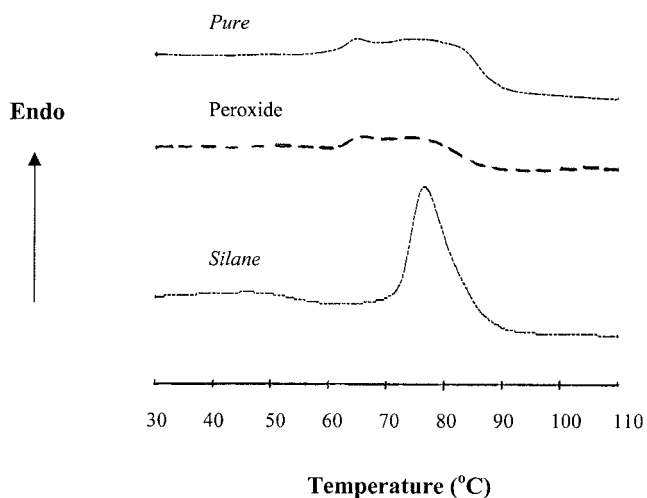[a] Values in parentheses are standard deviations.

Figure 7 DSC heating thermograms of EOR and its crosslinked samples.

the amorphous part of the material.[29] Therefore, a network obtained had a structure that differred completely from that of a network formed by means of peroxide crosslinking at the temperature high above the melting temperature.[29] Furthermore, the peroxide network is made from C–C linkages whereas the silane-crosslinked sample is characterized by the Si–O–Si bonds. Compared to the C–C bond, the Si–O–Si bond angle permits very free rotation about the Si–O bond.[30] The silane-crosslinked sample has, therefore, higher chain extensibility and flexibility than the peroxide-crosslinked one.

Melting and crystallization behaviors

In this part, melting and crystallization behaviors of peroxide-crosslinked and silane– water-crosslinked samples were compared. Figure 7 shows DSC thermograms of pure, peroxide-crosslinked, and silane–water-crosslinked samples. Pure EOR exhibits a broad differential scanning melting endotherm in which a melting temperature (T_m) ranging from 60 to 85°C is observed. The broad endotherm observed in this sample is due to the distribution in length of crystallizable ethylene sequence imposed by the placement of noncrystallizable comonomer units along the chain, leading to a broad distribution of crystal sizes in this polymer. A similar melting endotherm is observed for the peroxide-crosslinked sample. Differences in thermal behaviors can be seen in the case of silane–water-crosslinked samples. A sharp melting endotherm with a T_m of 78°C is clearly seen. It is believed that the recrystallization of polymer chain segments that are long enough to crystallize occurs during the crosslinking process (annealing effect).

Thermal stability and energy storage capacity

One of the main objectives for crosslinking polymers is to raise the upper service temperature limit of the

materials or to produce the materials that are thermally stable and do not undergo melt flow even when heated above the crystalline melting point. In some applications, such as off-peak electrical power for heating and cooling units, heat exchanger, etc., a material with high thermal-energy storage capacity is needed. in general, although crosslinks can eliminate melt flow, which is desirable for thermal form stability, they also decrease polymer crystallinity and heat of fusion, which is undesirable for high energy storage.[31] Therefore, it is of interest to compare the thermal stability and energy storage ability of the crosslinked products prepared using peroxide- and silane–water-crosslinking techniques.

The dimensional stability of crosslinked products upon heating in an air oven is investigated. The results are shown in Figure 8. After heating in air oven at its melting temperature ($T \sim 80°C$) for 5 min, pure polymer deforms and becomes very soft. In contrast, the samples obtained from both peroxide and silane–water crosslinking can retain their original shape and dimension. However, by increasing the temperature to 90°C, a peroxide-crosslinked sample shrinks and, when it is heated at 200°C for 5 min, the shrinkage and distortion are severe. In the case of the silane-crosslinked sample, no change in sample appearance is observed. There is only a slight change in dimension when heated at 200°C.

The thermal stability of the silane-crosslinked sample can also be observed via its flow properties. The flow properties are investigated here using the MFI measurements. Table III shows the MFI results of various crosslinked samples. For peroxide-crosslinked samples, the MFI value dropped sharply when the sample contained only 0.4% gel. This value decreased further when the content of gel increased and reached 0.1 g/10 min in the sample with 19% gel. Unlike peroxide-crosslinked samples, the silane-crosslinking network showed a stronger effect on melt viscosity. No flow was observed even in the sample containing 10% gel.
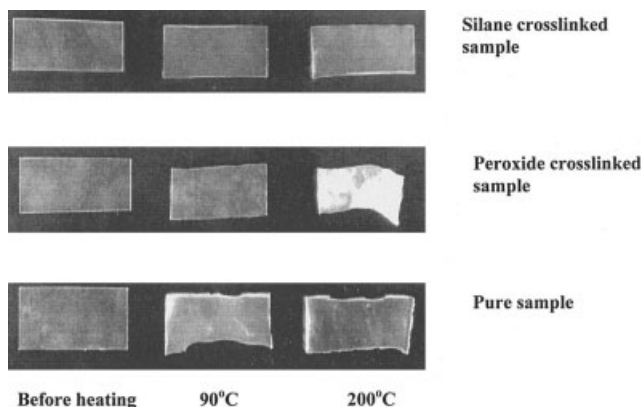

Figure 8 Thermal stability of EOR and its crosslinked, samples after heating in an air oven.

TABLE III
MFI and ΔH_f Retained of Various Crosslinked Samples

Peroxide crosslinking			Silane crosslinking		
Gel content (%)	MFI (g/10min)	ΔH_f retained (%)	Gel content (%)	MFI (g/10min)	ΔH_f retained (%)
Pure	64.8	100	Pure	64.8	100
0.4	13.0	94	10	0.0	91
16	0.2	78	71	0.0	91
19	0.1	77	77	0.0	91

As mentioned earlier, one of the drawbacks of crosslinking is a reduction in polymer crystallinity and heat of fusion (ΔH_f). In this study, the effect of the crosslink on the retention of ΔH_f (% ΔH_f retained) is investigated for the two different crosslinking systems. The results are shown in Table III, where the percentage retention of ΔH_f (% ΔH_f retained) can be calculated as follows.

$$\% \Delta H_f \text{ retained} = \frac{\Delta H_f \text{ of crosslinked sample}}{\Delta H_f \text{ of pure polymer*}} \times 100 \quad (2)$$

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

For peroxide-crosslinked samples, the % ΔH_f retained decreases systematically with an increase of gel content. The value of % ΔH_f retained drops to 77% when the sample contains only 19% gel. This behavior is undesirable for high thermal-energy storage applications. In the case of silane–water-crosslinked samples, a higher value of 91 for ΔH_f retained was observed in the sample containing 77% gel.

From the mechanical and thermal property results, it can be concluded that the silane-crosslinking technique gave a polymer of higher extensibility and better thermal stability and energy storage capacity than that produced by means of peroxide crosslinking. The silane-crosslinking technique is, therefore, more suitable for producing the crosslinked polymers for some applications that need a flexible and thermally stable material.

CONCLUSION

The crosslinking of metallocene EOR was studied. The crosslinked polymers were prepared using peroxide-crosslinking and silane–water-crosslinking techniques. It is found for peroxide crosslinking that an increase in DCP concentrations results in an increase of gel (degree of crosslinking). The maximum gel content obtained, however, is limited by its processing difficulty brought about by a significant increase in process torque and die pressure. After peroxide crosslinking, the tensile behaviors changed from uniform deformation and stress upswing at high strains, which are the elastomeric characteristics of the pure polymer to low extensibility and fracture at lower strains. In the case of silane–water crosslinking, these problems are eliminated. Compare to the peroxide-crosslinked samples, the silane-crosslinked polymers can be prepared with much higher gel contents. The silane-crosslinked polymers also showed remarkably higher extensibility and better thermal stability and energy storage capacity. The explanation for the differences between peroxide-crosslinked and silane-crosslinked polymers was proposed to be due to the structure of the crosslink network formed.

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