Changes in Properties of Silane–Water Crosslinked Metallocene Ethylene-Octene Copolymer After Prolonged Crosslinking Time

Kalyanee Sirisinha, Darinya Meksawat

Department of Chemistry, Mahidol University, Rama VI Road, Bangkok 10400, Thailand

ABSTRACT: The silane–water crosslinking of metallocene ethylene–octene copolymer is described. Particular consideration is made on the changes in mechanical, thermal, and rheological properties of crosslinked polymers after prolonged crosslinking time. The silane grafting is carried out in a twin-screw extruder, using a free-radical reaction of vinyl trimethoxysilane and dicumyl peroxide. The crosslinking reaction is conducted at 70°C in the presence of water. The results show that the rate of gel formation is very high in the early stage of crosslinking process and decreases thereafter. The maximum gel content of 77% is obtained after 60 h of immersing time. Increasing the immersing time beyond 60 h, the gel content does not increase further. However, the FTIR results reveal an increase in siloxane linkages in those samples, indicating an increase in crosslink density without a simultaneous increase in gel content. This finding is supported by a rheological study where a significant increase in storage modulus is clearly observed. As a result of denser network, movement and flexibility of polymer chains are more restricted, leading to some changes in tensile properties. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 901–906, 2004

Key words: crosslinking; ethylene–octene copolymer; properties; reactive extrusion; silane grafting

INTRODUCTION

Crosslinking is one important method for extending the useful range of commodity polymers to meet the demands of specialty applications. In addition to the typical peroxide crosslinking or irradiation crosslinking, the utilization of silane–water crosslinking has gained considerable attention in recent years not only for industrial applications such as cable insulation and water heating pipes,[1,2] but also in fundamental research,[3–12] because of its various advantages, such as easy processing, low capital investment, and favorable properties in the crosslinked materials. This process is based on the preparation of a silane-grafted polymer using peroxides and vinyl alkoxysilane in either solution or melt. After shaping into products, the silane-grafted polymer is crosslinked by exposure to a humid environment. The crosslinking reaction involves hydrolyzation of the hydrolyzable alkoxy groups with moisture, followed by condensation of the formed hydroxyl groups to form stable siloxane linkages.

Many studies were performed on the silane–water crosslinking of polyethylene (PE).[3–8] Shieh and Liu studied the silane-grafting reactions of various types of PE, including low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE).[3] They also investigated factors affecting the water-crosslinking reactions of the silane-grafted LDPE. These factors included time, temperature, morphology, and thickness of samples. The effects of these factors on the crosslinking rate and the resultant gel content were reported.[4] Narkis et al. studied the effect of catalyst on the crosslinking reaction by moisture of silane-grafted HDPE. The specimens with and without catalyst were compared. The results showed 70% gel in the sample with no catalyst after 400 h of crosslinking time. For the sample with catalyst, the crosslinking tendency was very high. The polymer was practically fully crosslinked (80% gel) in about 10 h under the same conditions.[5] Sen et al. studied the effect of the structures of three catalysts (i.e., stannous octoate, dibutyl tin dilaurate, and dialkyl tin mercaptide) on the moisture crosslinking of silane-grafted PE. The degree and rate of crosslinking were evaluated.[6]

To date, a few reports focusing on the properties of silane–water-crosslinked PE have been published in the literature. A decrease in elongation at break after crosslinking was reported by Hjertberg and coworkers for silane–water-crosslinked ethylene vinyl trimethoxysilane (EVS) copolymer.[7] In the work of Celina and George, some mechanical properties of silane–water-crosslinked LDPE were reported. However, most of

their work was concentrated on thermal and UV degradation of the crosslinked materials.[8] In our previous study, the peroxide-crosslinked and the silane–water-crosslinked ethylene–octene copolymers were compared. Clear differences between these two techniques, in terms of processing, and product mechanical and thermal properties were found.[9] The silane-crosslinked polymers were found to retain the elastomeric characteristics of the pure polymer and showed remarkably higher extensibility, better thermal stability, and better energy storage capacity.[9]

In the present article, we report some results on the effect of crosslinking time on silane–water crosslinking of metallocene ethylene–octene copolymer. Particular attention was made on the gel formation and the properties of the crosslinked polymers, including the mechanical, thermal, and rheological properties.

EXPERIMENTAL

Materials

Ethylene–octene copolymer (EOR) 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 dicumyl peroxide (DCP) initiator and vinyl trimethoxysilane (VTMS) were purchased from Aldrich (Milwaukee, WI) and were used without further purification.

Preparation of silane-grafted EOR

The silane-grafting process was carried out in a corotating twin-screw extruder (Prism TSE16), having two screws of 16 mm in diameter with an L/D of 20. 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 and peroxide used were kept constant at 5.0 and 0.1 phr, respectively. A screw speed of 30 rpm and the temperature profile of 160, 200, 200, 200, and 200°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 ($\sim$ 190°C) is less than 1 min.[13] The silane-grafted products obtained 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 for 5 min under pressure of 15 MPa. After cooling, a sheet was cut into tensile bars.

Preparation of water-crosslinked EOR

To conduct a crosslinking reaction, the samples were immersed in water at 70°C. The effect of time for crosslinking reaction was investigated. In this study,

no catalyst was used for accelerating the crosslinking reaction to avoid problems involving premature crosslinking during storage of the grafted products. From the work of Narkis et al., crosslinking of grafted HDPE containing 5% of catalyst was reported to occur during storage in a desiccator at 23°C. A gel content of 20% was obtained after only 25 h of crosslinking time.[5]

Characterization and testing

FTIR analysis of silane-grafted EOR

Fourier transform infrared (FTIR) spectroscopy was used to analyze the presence of silane in the grafted products and to follow the changes in amounts of methoxysilane groups (Si—OCH_3) and siloxane linkages (Si—O—Si) in the crosslinked polymers. 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 to remove unreacted silane or residual peroxide. The IR spectra were then recorded by using a Perkin–Elmer system 2000 FTIR spectrometer in the range of 600-4000 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 until constant weight, the gel content being defined as follows. At least three samples of each crosslinked polymer were used to yield three values of gel content, the average of which was then reported:

$$\% \text{ gel content} = \frac{\text{final weight of sample}}{\text{initial weight of sample}} \times 100$$

$$(1)$$

Tensile testing

An Instron tensile tester (model 4301) was operated at a crosshead speed of 500 mm min^{-1} by 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.
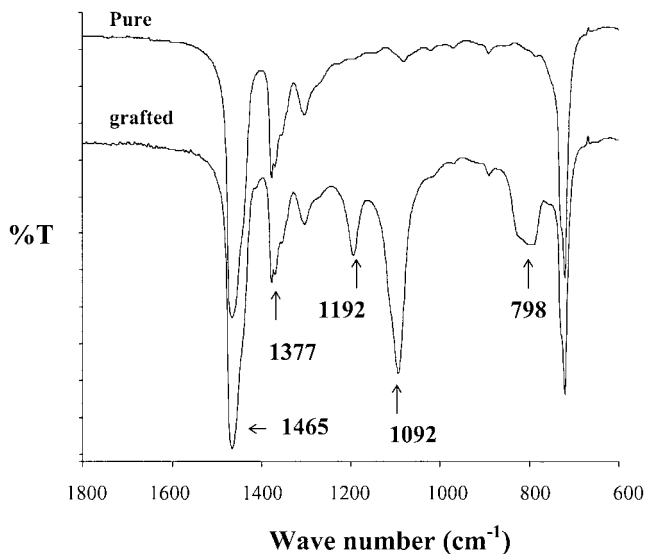
Figure 1 FTIR spectra of EOR samples before and after grafting reaction.

Differential scanning calorimetry (DSC)

To study the thermal behaviors of samples before and after crosslinking, 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^{-1}. The melting 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 % crystallinity.[14]

Rheological measurement

Dynamic rheological measurements were conducted with a parallel-plate rheometer (Physica MCR 500) with 25-mm-diameter plates and 1-mm gap wid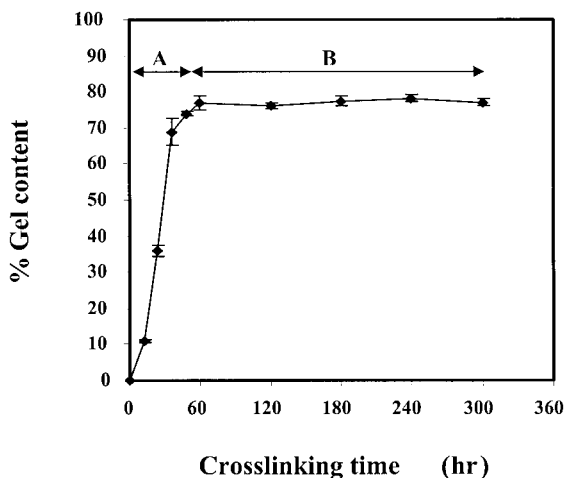th. The test was performed in an oscillatory shear mode at a constant strain of 10%. The range of frequency was from 1 to 200 rad s^{-1}. The measurement was carried out at 200°C. The shear storage modulus (G') and loss modulus (G''), as well as the complex viscosity (η^*), were determined.

RESULTS AND DISCUSSION

Evidence of grafting by FTIR

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 1 shows the FTIR spectra of EOR samples before and after grafting reaction. The characteristic peaks

Figure 3 Stress–strain curves of pure EOR and its silane crosslinked samples: crosslinking time (t) $\leq$ 60 h.

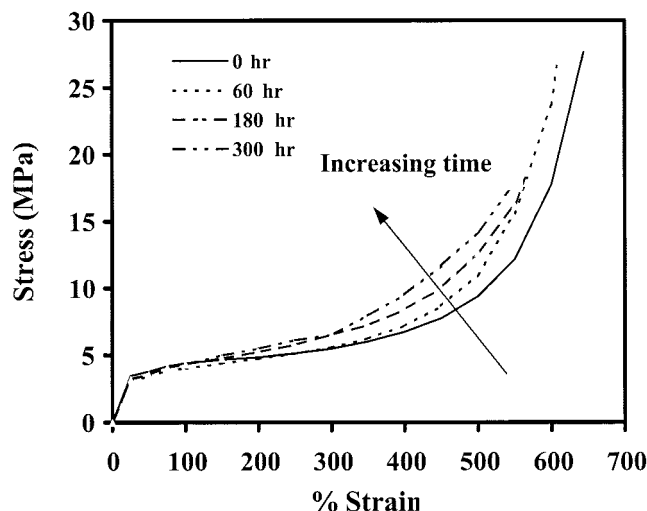**Figure 2** Effect of crosslinking time on the gel content.

Figure 4 Stress–strain curves of pure EOR and its silane-crosslinked samples: crosslinking time (t) $\geq$ 60 h.

TABLE I
Tensile Results of Silane–Water Crosslinked Samples

Time (h)	Strength at break (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)
0	27.64 ± 2.54	643.75 ± 10.30	4.43 ± 0.08	5.49 ± 0.11	9.37 ± 0.40
60	26.54 ± 4.00	607.90 ± 26.05	4.05 ± 0.11	5.60 ± 0.13	11.00 ± 0.53
180	18.66 ± 1.21	566.63 ± 12.18	4.35 ± 0.14	6.55 ± 0.44	12.63 ± 0.85
300	17.28 ± 2.02	543.20 ± 11.73	4.35 ± 0.12	6.50 ± 0.44	14.17 ± 0.36

observed at 1377 and 1465 cm^{-1} correspond to the C—H bending vibrations of the methyl and methylene groups of EOR, respectively. After the silane grafting reaction, three additional peaks corresponding to the trimethoxy silane group [Si—(O—CH$_3$)$_3$] in the samples were observed at 798, 1092, and 1192 cm^{-1}.

Water-crosslinking of silane-grafted EOR

Figure 2 shows the plot of water immersing time against the resultant gel content. The plot may be divided into two regions (i.e., region A and B). In region A, the gel content was observed to increase sharply with an increase of crosslinking time (t). The slope of the graph is very steep in the early stage of crosslinking ($t < 36$ h), inferring a high rate of gel formation in this stage. Thereafter, the rate decreases ($36 \leq t \leq 60$ h) and the maximum gel content of 77% is reached after 60 h of immersing time. Increasing the immersing time beyond 60 h (region B), the gel content does not increase further. The achievable gel content of 77% is obtained.

Changes in properties after water-crosslinking

Usually, many important properties of crosslinked polymers vary with the gel content. For peroxide
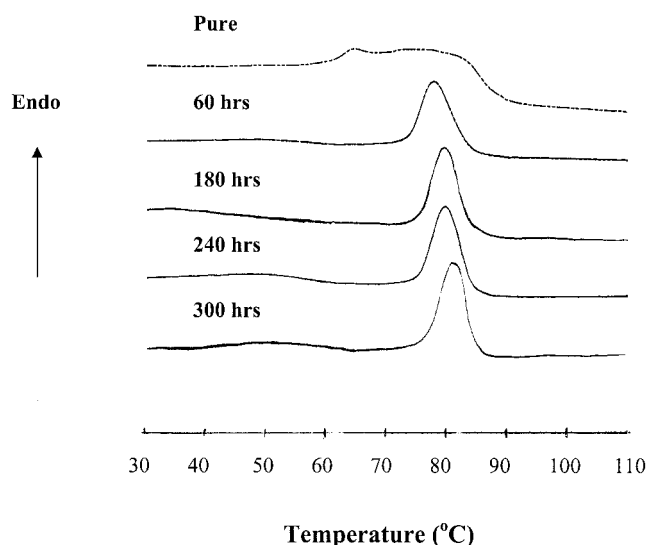

Figure 5 DSC thermograms of pure EOR before and after immersing in hot water for various times.

crosslinked polymers, a higher gel content was reported to result in a higher modulus and lower elongation at break.[7,9] In contrast to the peroxide crosslinking, the silane–water-crosslinked polymers showed very many similar mechanical properties to its pure polymer.[8,9] Figure 3 shows the stress–strain curves of pure EOR and its silane crosslinked products ($t \leq 60$ h). Both pure polymer and its silane-crosslinked samples show uniform deformation, high elongation, and stress upswing at high strains. No significant difference in the stress–strain curves is observed between samples containing various amounts of gel (10–77%). It is believed that for the silane–water-crosslinking process, similar to the irradiation process where the reaction occurred when the polymer was in the solid state, some inhomogeneity (uncrosslinked) may be present in the crosslinked network formed because of the limitation of polymer chain mobility involving in the reaction. The chains in these uncrosslinked regions are able to deform and behave similarly to those in pure polymer.[9,15]

Unlike Figure 3, the deviations in stress–strain curves can be seen in the case of samples crosslinked in hot water for more than 60 h. Although containing the same amount of gel (77%), these crosslinked samples show different properties (Fig. 4). Tensile strength and elongation at break decrease, whereas modulus at intermediate (100–300%) and high (>300%) strains increases with an increase of crosslinking time (Table I). The explanation for the differences in mechanical properties among those samples needs to be found out. Two possible reasons are proposed. The first one is due to the changes in mechanical properties of the EOR itself brought about by the annealing effect. During the crosslinking process, the samples were immersed in hot water for a long time. This may alter the polymer morphology (chain orientation and recrystallization) and, as a consequence, the mechanical properties change. The second reason is proposed to be due to an increase in density of crosslink network within the formed gel after prolonged crosslinking time. To verify these proposals, some experiments were carried out.

The pure EOR samples were subjected to the same conditions as used for the silane-crosslink process (i.e., immersed in hot water up to 300 h). The samples were then characterized by using DSC technique and tested

TABLE II
Tensile Results of Pure EOR Samples after Immersing in Hot Water for Various Times

Time (h)	Strength at break (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)
0	27.64 ± 2.54	643.75 ± 10.30	4.43 ± 0.08	5.49 ± 0.11	9.37 ± 0.40
60	25.35 ± 3.96	646.17 ± 28.27	4.12 ± 0.05	5.54 ± 0.07	9.01 ± 0.25
180	26.23 ± 3.54	670.23 ± 13.11	4.20 ± 0.09	5.46 ± 0.07	8.51 ± 0.14
300	25.82 ± 3.18	669.00 ± 17.70	4.16 ± 0.09	5.50 ± 0.11	9.04 ± 0.35

for the mechanical properties. Figure 5 shows the DSC thermograms of EOR before and after immersing in hot water for various times. Clear differences in DSC thermograms can be seen. Pure EOR (before immersing in hot water) shows a broad differential scanning melting endotherm with a melting temperature range from 60 to 85°C. 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; as a consequence, a broad distribution of crystal sizes in this polymer appear.[16] After immersing in hot water for a certain time, recrystallization of some chain segments that are long enough to crystallize is believed to occur, resulting in a sharp DSC peak with a melting temperature (T_m) of 78°C. However, this morphology alteration does not cause any changes in the tensile properties, as shown in Table II. The tensile properties of those samples are similar. From the DSC and tensile results, it seems to be possible to postulate that the changes in mechanical properties of the crosslinked samples after prolonged crosslinking time are not resulted from the morphology alteration due to annealing effect.

To investigate whether there is an increase in density of crosslink network in the samples after pro-

longed crosslinking time, FTIR was used to follow the changes in amounts of methoxysilane groups (Si—OCH$_3$) and siloxane linkages (Si—O—Si). As stated, in the crosslinking reaction, the methoxysilane groups were hydrolyzed and condensed to form siloxane linkages. An increase in siloxane linkages or a decrease in methoxysilane groups means an increase in crosslink density. By following any changes in these structures, a crosslink density can be determined. Generally, the bands of Si—OCH$_3$ groups are observed at 798, 1092, and 1192 cm^{-1}, and the Si—O—Si band can be seen at 1030 cm^{-1}, appearing as a shoulder on the larger band of Si—OCH$_3$ at 1092 cm^{-1} due to the Si—O bond in the Si—OCH$_3$. It is therefore difficult to make quantitative measurements of intensity of Si—O—Si band at 1030 cm^{-1}. The absorption bands of Si—OCH$_3$ at 798 and 1192 cm^{-1} were then followed. The results are presented as an absorption index, which is the relative intensity of the interested peaks at 798 and 1192 cm^{-1} to that of reference peak at 1377 cm^{-1}. Figure 6 shows a decrease in absorption index at 798 and 1192 cm^{-1} with increase in the crosslinking time. This indicates that there are more siloxane linkages formed without a simultaneous increase in gel content or, in other words, there is an increase in density or number of crosslink points in the already formed gel. The formation of crosslink
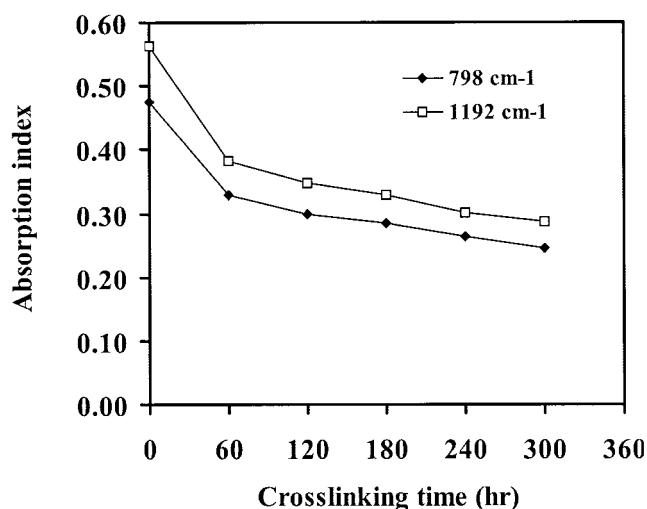

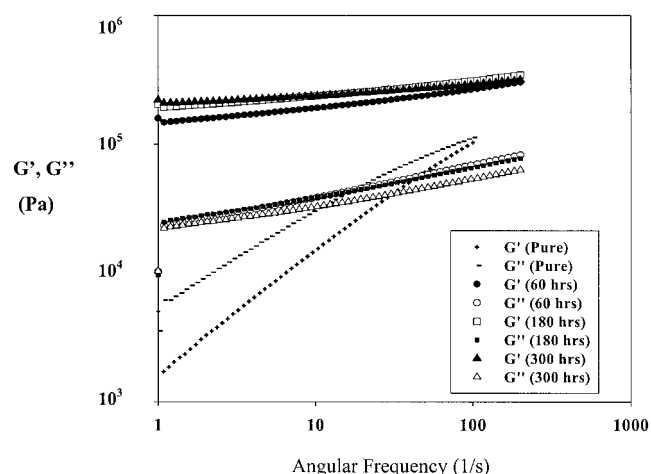**Figure 6** Changes in IR absorption index after prolonged crosslinking time.

Figure 7 Storage and loss modulus of pure EOR and its crosslinked samples.

TABLE III
Melting Temperature (T_m), Heat of Fusion (ΔH_f), and Percentage of Crystallinity (% X_c) of Various Silane–Water Crosslinked Samples

Time (h)	T_m (°C)	ΔH_f (J/g)	% X_c
60[a]	77	39	13.6
60	78	36	12.4
180	80	34	11.5
240	80	32	11.0
300	81	32	11.0

[a] Pure EOR sample after being immersed in hot water for 60 h.

linkages is believed to continue for a long time after the maximum gel was reached, resulting in a polymer with a tight network. This dense network, therefore, leads to a decrease in chain movement and flexibility; as a consequence, the modulus increases, whereas tensile strength and elongation at break decrease.

To confirm the increase in crosslinking points with an increase of crosslinking time beyond reaching the maximum gel content, a rheological test was performed. The viscoelastic properties of neat sample and silane-crosslinked samples were measured. Figure 7 shows the storage (G') and loss (G'') modulus as a function of frequency. The pure EOR sample shows a very strong frequency dependence of G' and G''. This behavior is a characteristic of uncrosslinked melts. The deformation is mainly viscous and hence the G'' values are higher than the G'. After crosslinking, the G' values increase significantly and exceed G'', indicating the dominating of elastic over the viscous responses. The values of G' are found to be higher than G'' throughout the frequency range studied. Both moduli show weaker frequency dependence when compared to those of pure polymer. The higher the crosslinking time, the higher the G' values, indicating the higher crosslink density.

Apart from the mechanical and rheological properties, the thermal behaviors change upon increasing the crosslinking time beyond reaching the maximum gel. Table III summarizes the DSC results of the samples crosslinked for 60 to 300 h. All these samples contain the same amount of gel at 77% but have different crosslink densities due to the difference in crosslinking time. It is found that the percentage of crystallinity (%X_c) and heat of fusion (ΔH_f) decrease, whereas T_m increases with increasing crosslinking time. This infers that crosslink network hinders the recrystallization of polymer chains during isothermal annealing. However, due to a very long crosslinking time, the chain segments which are able to crystallize form into a thicker crystal, resulting in an increase in melting temperature. The thickening of crystals after annealing was found also for ethylene–propylene block copolymer.[17]

CONCLUSION

This article presents the changes in properties of silane–water-crosslinked metallocene EOR after prolonged crosslinking time. The EOR was first grafted with VTMS in a twin-screw extruder, using DCP as an initiator. The grafted products were subsequently crosslinked in water at 70°C. The rate of crosslinking was very fast in the early stage and decreased thereafter. The maximum gel content of 77% was reached after 60 h of treatment time. Increasing the treatment time beyond 60 h, crosslink density increased without a simultaneous increase in gel content, as revealed by FTIR and rheological measurements. Crosslink network was found to hinder the recrystallization of polymer chains during crosslinking process. The mechanical test showed variations in tensile properties among silane-crosslinked samples. The samples crosslinked for less than 60 h exhibited similar tensile behaviors to the pure polymer where uniform deformation, high elongation, and stress-upswing at high strains were observed. The deviations in tensile properties were clearly seen in the samples crosslinked for more than 60 h. Although containing the same amount of gel, these crosslinked samples showed different properties. Tensile strength and elongation at break decreased, whereas modulus at intermediate and high strains increased with an increase of crosslinking time, due to the presence of denser network.

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