

# Structure Development and Viscoelastic Properties in Silane-Crosslinked Ethylene–Octene Copolymer

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**ABSTRACT:** The development of structure and viscoelastic properties during silane crosslink reaction in metal-ocene ethylene–octene copolymer has been investigated. Using attenuated and transmission infrared spectroscopy, the concentrations of certain functional groups and change in sample thickness were monitored, giving the information on the progress of crosslink reaction. The evolution of crosslink content and viscoelastic properties was analyzed using a parallel-plate rheometer. The results showed that crosslinking process started with the hydrolyzation of methoxy groups in the near-surface layer, proceeding in a diffusion manner. At this stage no silanol groups could be detected, revealing that the condensation occurred promptly after hydrolyzation. The internal crosslink could not begin until there are sufficient water molecules in the

surrounding. A water by-product from the condensation reaction played an essential part in the center region. The rheological data showed a reduction in magnitude of creep compliance. As the reaction proceeded, more networks took place within an existing gel. The materials, then, acted more like elastic and exhibited an improvement in ability for recovery process. The immobilization of chain segments, due to the presence of tight network, disallowed conformations necessary for crosslink reaction and a certain amount of hydrolyzable groups and silanol groups remained after a long crosslinking process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2347–2353, 2008

**Key words:** ethylene–octene copolymer; crosslinking; silane; structure; viscoelastic property

## INTRODUCTION

Silane–water crosslinking is one of the well-known techniques used in crosslinking polyethylene (PE).<sup>1–9</sup> It can also be used in the crosslinking of ethylene copolymer,<sup>10–14</sup> polypropylene,<sup>15–18</sup> polyvinyl chloride,<sup>19–20</sup> etc. The crosslinked products are mainly used in applications such as hot-water piping insulation, and wire-cable industry. The basic process starts with the preparation of a silane-grafted polymer by a free-radical grafting reaction of vinyl silane in the presence of peroxide. After shaping into product, the silane grafted polymer is then crosslinked by exposure to a humid environment. Since each Si atom has three reactive groups, up to six polymer macromolecules may be joined to each crosslink, which enhances the mechanical properties of the crosslinked products. This is unlike to other crosslinking methods, i.e., peroxide crosslinking and radiation crosslinking, where two macromolecules join in the crosslink network.

There are a number of published works concerning some of the basic properties change upon crosslinking. One of the major properties that could be improved by introducing a crosslink network into the system is the high temperature property. An improvement in polymer thermal stability due to silane crosslink is usually resulted. In the case of mechanical properties, Shah and coworkers reported an improvement in tensile strength with increasing silane content up to 5%. The resultant product showed the gel content of about 60%.<sup>7</sup> A similar result was found by Wang and coworkers,<sup>13</sup> where an increase in tensile strength and a drop in elongation at break were observed with increasing the crosslinking degree. However, there are studies reaching some contradictory results. For example, Celina and George found only slight decrease in polymer extensibility in the crosslinked LDPE containing a high gel content of 90%.<sup>6</sup> In our previous work on silane crosslinked ethylene–octene copolymer (EOR), no significant difference in tensile properties was found in the samples containing gel in the range of 0–77%.<sup>10</sup> The questions, therefore, arise from the attempt to describe the properties of these crosslinked materials. One of which is related to the structure of crosslink network presence in those crosslinked materials and the effects caused by crosslink structure.

The aim of the present work is to gain more understanding on the development of structure

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during silane crosslink reaction in metallocene ethylene–octene copolymer and the changes in viscoelastic properties along the progress of reaction. To achieve this aim, 6-mm thick samples of silane-grafted polymer were crosslinked in hot water for a specified time in the absence of catalyst. The samples were then sectioned into equally five layers for analysis. Using attenuated and transmission FTIR technique allowed us to follow the changes in the concentrations of certain functional groups as a result of crosslink reaction. These structural changes were analyzed together with the evolutions of crosslink content and viscoelastic properties obtained from the parallel-plate rheological measurements.

## EXPERIMENTAL

### Materials

Metallocene ethylene–octene copolymer; EOR (Engage E8003) with an octene content of 7.6% mole and an MFI of  $1.0 \text{ g} \cdot 10 \text{ min}^{-1}$ , was purchased from DuPont Dow Elastomer Co. (Wilmington, USA). Its molecular weight and molecular weight distribution are  $\sim 150,000 \text{ g mol}^{-1}$  and 2.3, respectively. The peroxide and silane used were dicumyl peroxide (DCP) and vinyl trimethoxysilane (VTMS), respectively. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, MI) and used without purification.

### Crosslinking of EOR

The silane-grafting reaction of EOR was carried out in molten state using a corotating twin-screw extruder (PRISM TSE16, Staffordshire, UK). The concentrations of peroxide and silane used in the reaction were kept constant at 0.1% and 5.0% weight, respectively. A screw speed of 30 rpm with a temperature profile of 160, 200, 170, 170, and  $170^\circ\text{C}$  from feed zone to die zone was carefully controlled. The total reaction was finished within 5 min. During the modification process, the main reaction is silane grafting. However, other reaction is also possible such as combination of polymer macroradicals which produces molecular crosslinks. In this study, no evidence of gelation due to the self-crosslinking was observed in our grafted products. The grafted products obtained were then compression-molded into 6-mm thick sheets. The molding temperature used was  $190^\circ\text{C}$ . To conduct a water-crosslink reaction, the molded sheets were immersed in hot water at  $70^\circ\text{C}$  for a specified time. The samples were then sectioned into equally five layers before analysis. It needs to be mentioned here that no catalyst was used for accelerating the crosslinking reaction in this study.

### Measurements

Attenuated (ATR) and transmission (TS) Fourier Transform Infrared (FTIR) Spectroscopy was used here to analyze the presence of silane in the grafted products and also to follow the progress of crosslink reaction. The IR spectra were recorded using a Perkin–Elmer system 2000 FTIR spectrometer (Boston, MA) in the range of  $600\text{--}4000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ .

The gel fraction was determined by the content of insoluble fraction of crosslinked material after solvent extraction according to ASTM D2765-01. 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 samples were weighed after being dried in a vacuum oven at  $55^\circ\text{C}$  until constant weight. The gel content was calculated using the following equation.

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

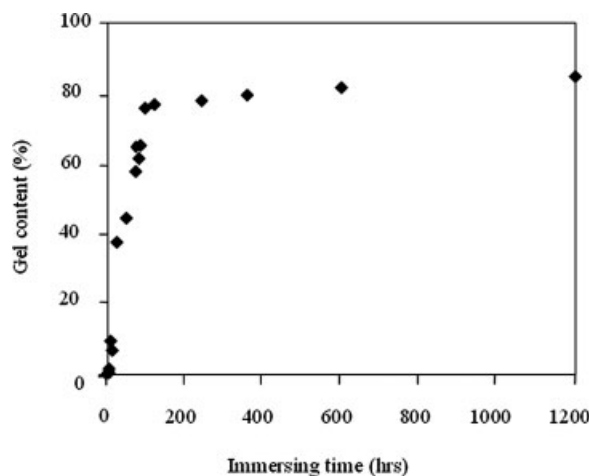
The percentage of gel reported in this work is an average of those obtained from three test results.

The parallel-plate rheometer (Physica MCR 500) was operated in an oscillatory shear mode at a constant strain of 10%. The samples used in the test were fabricated in a disk with 1 mm in thickness. The rheological behaviors were examined at  $200^\circ\text{C}$  under the frequency ranged from 1 to  $200 \text{ rad s}^{-1}$ . The resultant storage ( $G'$ ), loss ( $G''$ ), and complex modulus ( $G^*$ ) values were recorded. For the creep and recovery test, the applied stress was first hold constant at 1000 Pa for 300 s at a frequency of 1 Hz and a test temperature of  $200^\circ\text{C}$ . The resultant strain deformation was then recorded. The ratio of strain values measured and constant stress was calculated, defining as the creep compliance ( $J$ ). After the removal of stress, the strain recovery was examined from the plot of strain as a function of time.

## RESULTS AND DISCUSSION

### Amount of crosslinking

Some selected crosslinked EOR samples were characterized to determine their gel content and crosslink density. Figure 1 shows the evolution of the amount of gel with the time of crosslink reaction. A continuous increase in the gel content is observed with increasing crosslinking time up to about 100 h. The increase in gel content with time is generally observed in various crosslinked systems.<sup>7-9,15</sup> The rate of crosslink reaction, as determined from the slope of the graph, is faster in this early stage of crosslinking.



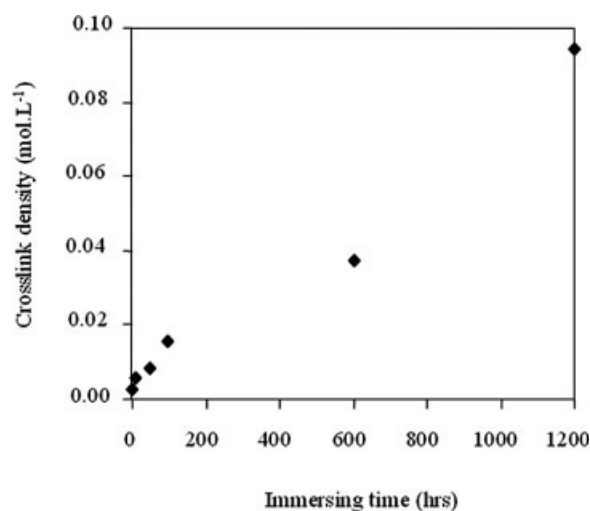
**Figure 1** Evolution of gel content as a function of crosslinking time.

Without catalyst, the EOR reaches 80% gel after 96 h. of crosslinking time. Increasing the time further, the gel contents tend to level off. Another effective way of characterizing crosslink network is by determining crosslink density ( $\nu$ ). This method was reported to be successful in determining the crosslink content of LDPE crosslinked by irradiation process.<sup>21</sup> Based on the theory of elasticity, the number of crosslink in a unit volume or crosslink density can be predicted using the following equation.

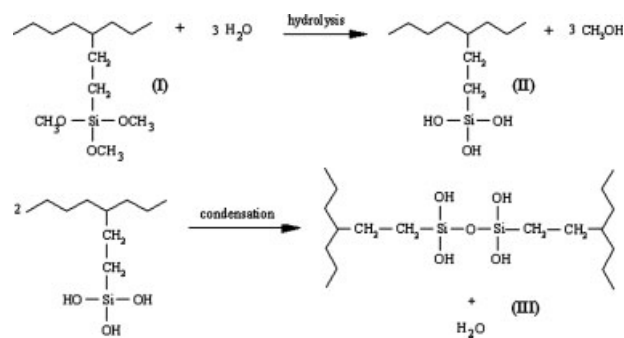
$$G^* = \nu RT \quad (2)$$

where  $G^*$  is complex modulus,  $R$  is gas constant, and  $T$  is temperature.

The calculated crosslink density of EOR at 20 rad s<sup>-1</sup> is shown in Figure 2, where a systematic increase in crosslink density with increasing time is clearly illus-



**Figure 2** Crosslink density as a function of crosslinking time.



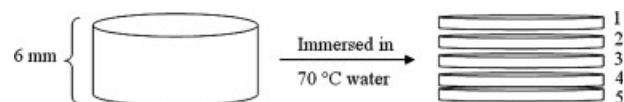
**Figure 3** Silane-water crosslink reaction.

trated. The graph of crosslink density does not show a plateau region as observed in the gel results (Fig. 1). The differences of gel and crosslink density data will be discussed later in this article.

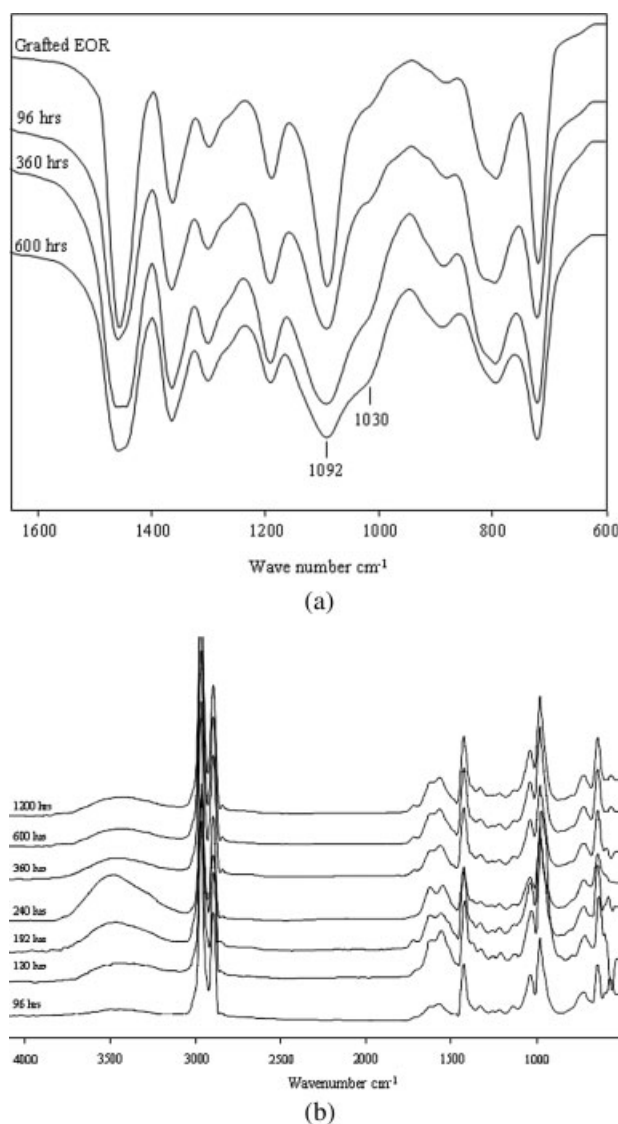
### Crosslink structure development

The crosslinking of semicrystalline polymer in the solid state is quite a complex process. Several factors may influence the crosslink reaction. The chemistry of silane crosslink is shown in Figure 3. The first reaction begins with the hydrolyzation of methoxysilane (Si—OCH<sub>3</sub>) moieties (structure I) to form silanol (Si—OH) groups (structure II) and gives methanol as a by-product. In the second reaction, the formed silanol groups condense and produce siloxane (Si—O—Si) linkages (structure III), giving water (H<sub>2</sub>O) as a by-product. In this study, it is of interest to find out whether this H<sub>2</sub>O by-product involves in the crosslink reaction and how difference in crosslink density is among various regions in the crosslinked samples. To achieve this aim, a crosslink reaction was performed on a 6-mm thick specimen. After sectioning equally into five layers as shown in Figure 4, each layer was analyzed for the changes in IR peak intensities of certain chemical structures. Layer 1 and 5 represent the two layers which have large contact surface with water. Therefore, the hydrolyzation and condensation reactions are expected to proceed more rapidly in these two layers, compared to those in Layer 3 which is in the center. In addition, Layer 1 and 5 are expected to have similar behaviors. This expectation also goes to Layer 2 and 4.

Figure 5(a,b) illustrate examples of FTIR spectra of EOR samples crosslinked for various times obtained from TS and ATR modes, respectively. Table I sum-



**Figure 4** Thick specimen used in this study.



**Figure 5** FTIR spectra of crosslinked EOR samples obtained from TS mode (a), and ATR mode (b).

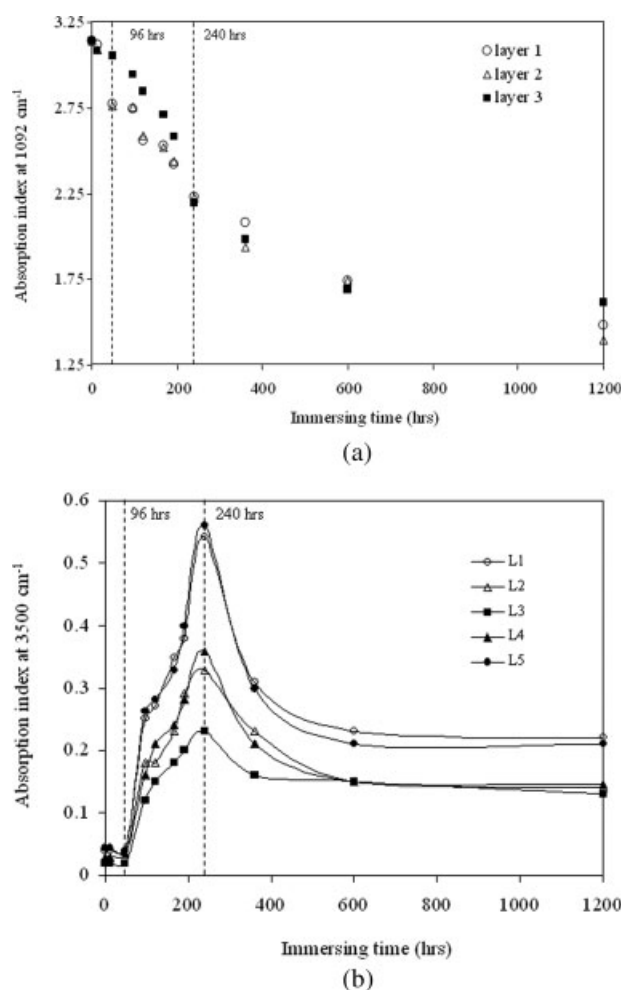
marizes the absorption frequencies generally used to follow the crosslink reaction. In the case of Si—OCH<sub>3</sub>, its evaluation is quite straightforward in which a decrease in its peak intensity clearly reveals a progression in hydrolyzation of structure I. The peak of Si—OCH<sub>3</sub> (at 1092 cm<sup>-1</sup>) from the spectra in ATR mode is quite small therefore the results on the changes in Si—OCH<sub>3</sub> groups at 1092 cm<sup>-1</sup> were followed by TS-FTIR. For the two others (Si—O—Si and Si—OH), the situation is more complicated. The

**TABLE I**  
Absorption Frequencies Used in Following Silane Crosslink Reaction

Chemical structure	Wave number (cm <sup>-1</sup> )
Si—OCH <sub>3</sub>	1092
Si—OH	3500
Si—O—Si	1030

absorption of Si—O—Si (at 1030 cm<sup>-1</sup>) appears as a shoulder on the larger band of Si—OCH<sub>3</sub>, this makes difficulties in quantitative measurements of intensity of the Si—O—Si band. In the case of Si—OH intensities, the FTIR results from both TS and ATR modes show similar trend. However, the Si—OH peak (at 3500 cm<sup>-1</sup>) is much clearer from the measurement in ATR mode. Therefore, the results of Si—OH changes based on the ATR mode are presented in this article. All results from both TS-FTIR and ATR-FTIR are presented in a term of absorption index, which are determined by calculating the ratio of absorbance of the interested bands, to the absorbance of the methyl group band at 1377 cm<sup>-1</sup>, which was used as the internal reference in the normalization of different spectra. The reported values were obtained, averaging at least five measurements in different points of the samples.

The infrared results are shown in Figure 6(a,b) where the absorption index of Si—OCH<sub>3</sub> group (at 1092 cm<sup>-1</sup>) and Si—OH group (at 3500 cm<sup>-1</sup>) are



**Figure 6** Absorption index of Si—OCH<sub>3</sub> group at 1092 cm<sup>-1</sup> (a), and Si—OH group at 3500 cm<sup>-1</sup> (b) in different layers as a function of crosslinking time.

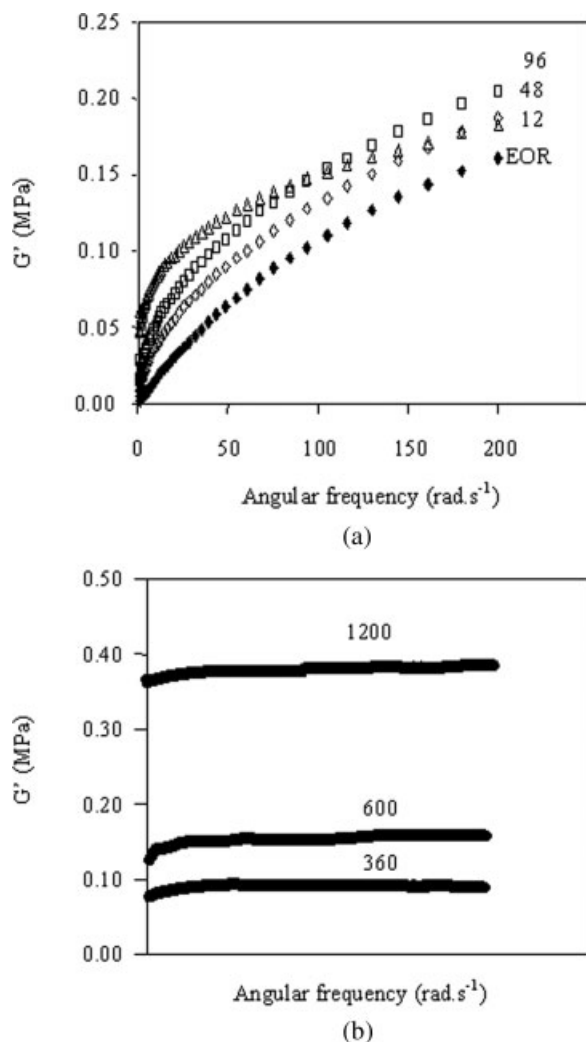
plotted against the time of crosslink reaction, respectively. In Figure 6(a), only the results of Layer 1, 2, and 3 are shown in the graphs, due to a large number of data points and a similar behavior between Layer 1 and 5, and between Layer 2 and 4 as mentioned earlier. The absorption index of Si—OCH<sub>3</sub> peak in all layers does not seem to change after 12 h of crosslink reaction, implying the very slow rate of hydrolysis of this material. An evitable change can be seen after conducting a reaction for 48 h. With increasing the time of reaction further, a gradual decrease in Si—OCH<sub>3</sub> absorption index is clearly seen. Similar trend can be observed in all layers but the magnitudes of these absorption values are different among layers. This reveals a heterogeneous crosslink formation in the samples. This is possible since the silane-crosslink reaction occurs when the polymer is in solid state. Heterogeneous crosslink structure is now generally accepted also in irradiation of PE in the solid state.<sup>22</sup>

At 96 h of crosslinking time, a drastic decrease in the absorption values of the Si—OCH<sub>3</sub> is obvious in the samples of Layer 1 and 2 (also Layer 4 and 5, the results are not shown here). This means that the hydrolyzation of Si—OCH<sub>3</sub> to form Si—OH has taken place in these two layers (1 and 2). However, when analyzing the data of Si—OH index in Figure 6(b), no increment or any changes in peak intensities of Si—OH could be detected at this stage (96 h of crosslinking time), illustrating that no Si—OH structure exists in the samples. This points out that after the hydrolyzation of Si—OCH<sub>3</sub> to form Si—OH, the formed Si—OH may possibly undergo further reaction (condensation) and then exists as Si—O—Si crosslink structure. In the case of Layer 3 which is in the interior of the specimen, the Si—OCH<sub>3</sub> absorption as shown in Figure 6(a) does not seem to change much even after conducting a reaction for 96 h. One possible explanation could be the lack of water to aid hydrolyzation in the surroundings. The reduction in Si—OCH<sub>3</sub> intensities in the center region of the specimen becomes more drastic than the other layers when increasing the crosslinking time to 240 h. It seems obvious that the hydrolyzation in this center region is not controlled only by the amount of water diffused from the outside. The water by-product from the condensation reaction also promotes the hydrolyzation of Si—OCH<sub>3</sub> in this region. At this stage, the absorption index of Si—OH reaches maximum value. In the other words, there are now a large number of silanols in the samples which are available for the condensation reaction. The similar findings are found also for the surface and near-surface layers. An increase in water diffusion from the outside causes further increase in the hydrolyzation of Si—OCH<sub>3</sub> to form Si—OH. However, all the Si—OH formed could not completely undergo condensation reaction, possibly due to the

restriction of polymer chain movement caused by the presence of crosslink network formed previously. As a result, a large number of Si—OH groups are detected at this stage of crosslinking time. The presence of Si—OH peak is found also even after 1200 h of crosslinking time, revealing that some hydrolyzed groups are actually left to be further condensed to form siloxane crosslink network. Whether a large number of these reactive groups are left cannot be said, but it is clear that they are unable to find a suitable partner for a condensation reaction. Not only the Si—OH group, but also the Si—OCH<sub>3</sub> still exists after a long reaction time ( $t > 1200$  h). Unreacted Si—OH and Si—OCH<sub>3</sub> groups could be present due to their steric hindrance, thus it is difficult for whole active groups to completely react.

Evaluating all this information, the progress of silane-water crosslink reaction is proposed as followed. In the first stage, the hydrolysis and condensation reactions initiate mostly in the layers in contact to water and layers nearer to the polymer surfaces. The interior layer seems to be unchanged for a long time after conducting the experiment. The diffusion of water into polymer is believed to play a major role in controlling the degree and rate of hydrolyzation. Therefore, any factors promoting water diffusion will increase the reaction. With semicrystalline polymers, the crystalline regions are less accessible to water which must diffuse in to be effective. The hydrolyzation and condensation, therefore, preferably occur in the amorphous part. Our previous findings revealed that the samples with lower crystalline component gave higher gel content and higher water diffusion rate.<sup>9</sup> The work of Shieh et al. on water crosslinking of silane-grafted LDPE demonstrated an increment in water diffusion rate and subsequently hydrolysis and condensation rates of the silyl trimethoxy moiety with increasing temperature.<sup>8</sup> In addition, hydrolyzation leads to the formation of hydrophilic chemical species, i.e., methanol in this case. This makes them accessible to water. Once the Si—OCH<sub>3</sub> groups in the surface and near-surface layers have been hydrolyzed, they condense and form Si—O—Si linkage promptly and released water as a by-product. This mechanism undergoes in the near-surface layers for a period of time and thereafter, the reaction in the center layer begins when there is a sufficient amount of water presence. The water involved in the reaction is believed to be the one diffused from external source through the near-surface layers and that produced as by-product from the condensation reaction. This, therefore, causes a rapid reduction of Si—OCH<sub>3</sub> intensities in the center region. By this period of time, the material should be characterized by a large number of crosslink networks.

Increasing the crosslinking time further, (e.g.,  $t > 240$  h) the hydrolyzation and condensation reactions



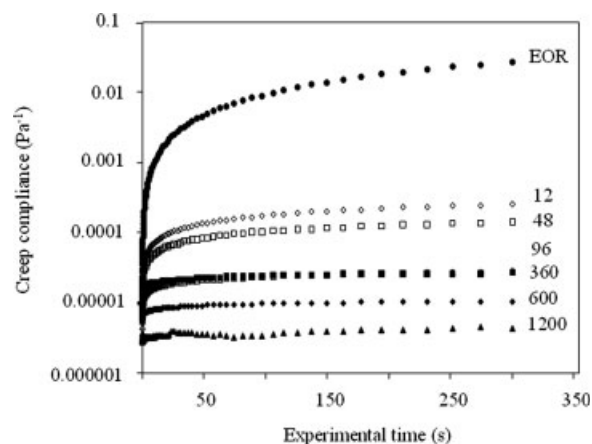
**Figure 7** Comparison of storage modulus ( $G'$ ) among various samples crosslinked for  $t \leq 96$  (a) and  $t > 96$  h (b).

still carry on so long as water is present in the system but with a much lower rate. In this stage, a tight network is believed to take place within an existing gel. This is the reason why we could not observe a systematic increase in the gel content in this latter stage since the weight of polymer gel is hardly changed but the number of crosslink points within the gel increases. The rheological results clearly confirm this point where an increment in crosslink density progresses with time of reaction. Because of a tight crosslink network, the diffusion of potential waters decreases. Decreased water diffusion will also increase the hydrolysis resistance of crosslinked system. Furthermore, crosslinking also immobilizes segments which disallow conformations necessary for chain combination. As a result, there are a number of silanol groups which cannot continue the condensation reaction and some hydrolyzable groups left for the crosslink reaction.

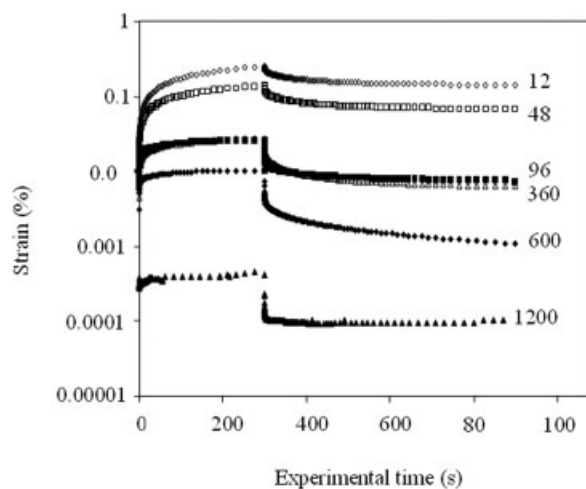
### Creep behaviors of crosslinked EOR

To further elucidate the effect of crosslink structure on polymer behaviors, rheological experiments using a parallel-plate rheometer were performed. The results obtained are illustrated in Figure 7(a,b) which are the plot of  $G'$  of the neat EOR and its modified as a function of frequency. A very strong frequency dependence of  $G'$  of the neat sample indicates the domination of viscous response which is a characteristic of uncrosslinked melt. After conducting a crosslink reaction, the flattening of  $G'$  indicates that the samples in the present experiment were crosslinked from lightly to heavily. For the samples crosslinked for very long time ( $t \geq 360$  h) as illustrated in Figure 7(b), a frequency independence of  $G'$  which is the characteristic of fully elastic material is clearly observed, inferring the presence of much denser network in the system. Not only a frequency independence of  $G'$ , but an increase in modulus is also revealed.

Figure 8 illustrates the plot of creep compliance ( $J$ ) of EOR before and after conducting a crosslink reaction, as a function of experimental time. It is evident that all crosslinked polymers exhibit much lower magnitudes of  $J$ , compared to the unmodified EOR sample. A difficulty in polymer chain mobility caused by the presence of crosslink network should be responsible for this behavior. With increasing the crosslinking time, a reduction in  $J$  magnitude becomes more pronounced, indicating an improvement in strength of the materials. The effect of crosslink network on material deformation can be seen also from the results of Figure 9, where crosslink network offers a difficulty in chain deformation. A drastic snapback is observed after a stress removal, acting more like elastic. As increasing the crosslinking time, the network becomes denser and stronger leading to an improvement in ability for recovery process.



**Figure 8** Comparison of creep compliance ( $J$ ) among various crosslinked samples.



**Figure 9** Strain deformation of various crosslinked samples as a function of experimental time.

## CONCLUSIONS

Silane-water crosslinking of EOR was performed in the solid-state without the presence of catalyst. The crosslink density linearly increases with increasing the time of crosslinking, while the gel results show an increment in the early stage and then level off. Infrared spectroscopy reveals a heterogeneous crosslink network in the system. In the first stage of crosslinking process, the hydrolysis event proceeds in a diffusion manner, starting at the regions nearer to the polymer surface. Once the hydrolyzation occurs, the formed silanol group continues further reaction (condensation) immediately and exists as siloxane crosslink network, giving water as a by-product. The internal crosslink cannot begin until enough water molecules have been existed in the surroundings. A water by-product plays an essential part in this region. After a long crosslinking

time, more networks take place within an existing gel. As a consequence, water diffusion decreases and immobilization of chain segments disallows conformations necessary for crosslink reaction. There are a number of hydrolyzable groups and silanol groups remained in the samples for further reaction. As the network becomes denser, improvements in material strength and ability for recovery process are resulted.

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