Differential Scanning Calorimetry (DSC)

To study the effect of crosslink on crystallisation and structure of EOR blends, the thermal behaviours of the samples before and after crosslinking were analysed using a Perkin-Elmer DSC-7 (Boston, MA). The test specimens (5 ± 1 mg) were heated from 50 to 150 °C at a scan rate of 20 °C.min^{-1}. The temperature was then maintained at 150 °C for 5 min before cooling to 50 °C at the same rate.

Thermal Gravimetric Analysis (TGA)

A Perkin-Elmer TGA-7 thermal gravimetric analyser (Boston, MA) 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, then heated to 600 °C at the rate of 20 °C.min^{-1}. The weight percentages of samples were measured as a function of temperature.

Thermal ageing test

The dumbbell specimens of 1 mm thick were stamped cut from a compression-moulded sheet and then crosslinked in hot water at 70 °C for 120 hr. The crosslinked specimens were then hang in a hot-air oven at 110 °C for 12 hr, before measuring their tensile properties. The tensile test was carried out using an Instron tensile tester Model 5569, with a crosshead speed of 500 mm.min^{-1} and a 1 kN load cell.

Results and discussion

Silane grafted EOR/LDPE blends

Figure 2 shows the FTIR spectra of unmodified EOR and silane-grafted EOR samples. The characteristic peaks of EOR at 1377 and 1465 cm^{-1} correspond 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 can be seen at 798, 1092, and 1192 cm^{-1}. The grafting index in various samples were determined by calculating 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 normalisation of the different spectra. The reported values were obtained, averaging at least five measurements in different points of the samples. The calculated grafting degree of EOR, LDPE, and their blends demonstrated in Table 1 shows only slight difference among these samples. Considering the energy required for bond breaking, the homolytic bond dissociation energies for hydrogen attached to primary, secondary, and tertiary carbons are 410, 397, and 385 $kJ.mol^{-1}$, respectively. [18] Thus, the least energy needed for a free radical to abstract hydrogen is from a tertiary carbon among the three kinds of carbons. Compared the two polymers used, the LDPE has a long branch structure having the number of branch in the range of 20-30 methyl groups per 1000 carbons. [18] In the case of EOR which is one of the LLDPE groups, it usually has the number of short chain branching in the range of 20-50 methyl groups per 1000 carbon. [19] For the LLDPE with a similar octene content to that in the EOR used in this study (7 %mol), Parent et al. reported a structure with 31 tertiary carbons per 1000 carbons. [20] Due to a similar structure between the two polymers used in this study and a small amount of silane (5%) used in the reaction, only slight difference in grafting degree is found among various blend compositions.

Crosslinking of silane-grafted EOR/LDPE blends

After conducting a crosslink reaction in water, the contents of gel in various EOR/LDPE blend samples were determined as a function of immersing time. As expected, the content of gel increases with increasing the crosslinking time (Figure 3). All samples show similar trend but with different magnitudes of gel content obtained. Although containing similar grafting degree, the EOR yields a higher gel content of 85 % while the LDPE shows only 67 % gel after 600 hr of crosslinking time. In the blend systems, the maximum contents of gel decrease with increasing the LDPE concentrations, i.e. 83, 81, 80 % gel in the case of 90/10, 70/30, and 50/50 blends, respectively. In this study, a linear relationship is observed between crosslink content and amount of crystalline component in the blends shown in Figure 4. Not only the crosslinking degree, but also the rate of crosslinking varies among the blend samples. For a particular blend, the crosslinking rate is comparatively high in the early stage of crosslinking process and slows down thereafter. By analysing the slope in the initial stage of the graph, the crosslinking rate can be estimated. The rate of crosslinking of EOR is approximately 6 times higher than that of LDPE. Substitution of EOR by LDPE in the blend, therefore, causes some changes in crosslinking rate. As a content of LDPE in the blends increases, rate of crosslinking decreases systematically. The reason for this observation is believed to be due to a lower rate of water diffusion in LDPE during the crosslinking reaction, brought about by its higher amount of crystalline portion.

Melting and crystallisation behaviours

The melting and crystallisation behaviours of EOR/LDPE blends are illustrated in Figure 5. The DSC results are summarised in Table 1. The unmodified EOR shows 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 length of crystallisable ethylene sequence imposed by the placement of non-crystallisable comonomer units along the chains, as a consequence, a broad distribution of crystal sizes in this polymer. In contrast to EOR, LDPE shows 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 is observed. This may be due to a variation in crystal sizes in the system. When increasing the LDPE concentrations further, the T_m peaks of the blends increase and shift toward the T_m of LDPE. Not only the T_m, but also the values of ΔH_f, T_c and $T_{c\ onset}$ increase systematically upon increasing the LDPE concentrations in the blends. The grafted silane shows only slight effect on the melting and crystallisation behaviours of the blends as shown in Table 1.

Figure 6a demonstrates the DSC heating thermograms of EOR samples before and after conducting a crosslinking reaction. It is interesting to see a sharp melting endotherm of the crosslinked EOR sample showing a T_m peak at 87 °C, which is unlike to that observed for the unmodified EOR sample. These results infer that recrystallisation of some chain segments may occur during conducting a crosslinking reaction and leads to some changes in polymer microstructure. To verify if the conditions used in the crosslinking process induce changes in crystal structure of the silane-grafted polymers and how do the crosslinking and crystallisation processes interfere with each other, some selected samples were annealed under the same testing condition as that used in the crosslinking process. The DSC analyses on the annealed samples were then carried out. An endotherm which is similar to that observed for the crosslinked product is clearly seen in the annealed sample. During a long crosslinking time, any chain segments that are long enough to crystallise have sufficient time for recrystallisation process and form into a more well-defined crystal structure. This finding is also observed in the blend systems. Clearly, the split of the T_m peaks of EOR and LDPE is observed in the DSC thermograms of the 70/30 and 50/50 blends. Example of DSC thermogram of the crosslinked 70/30 blend is shown in Figure 6b. The crosslinked samples and annealed samples of all blend series show only slight difference in the T_m, T_c, $T_{c\ onset}$, and ΔH_f values (Table 2). This suggests an important point that silane crosslink does not disturb the recrystallisation process of the blends. Silane crosslink is, therefore, believed to preferentially take place in the amorphous region.

Thermal stability and energy storage capacity

An investigation on thermal stability of the crosslinked products using thermogravimetric analysis (TGA) was performed. The decomposition temperatures (T_d) of all blends before and after crosslink are shown in Table 2. The decomposition temperature of EOR is observed at 473 °C, whereas LDPE shows the decomposition temperature at 490 °C. By incorporating LDPE into the system, the decomposition temperatures of the blends shift slightly to higher temperatures. The thermal degradation undergoes and completes at around 550 °C, with no residue at the end of the degradation. The presence of silane crosslink increases the decomposition temperatures of the blends to some extent, in particular those with higher concentrations of EOR. Insignificant increase in the decomposition temperature is found for LDPE system. This could be due to a lower degree of crosslinking in this system, compared to that in EOR. Correlations between thermal stability and crosslink density have been studied with contradictory results in the literature. [21-23] For peroxide-crosslinked system, Krupta and Luyt reported a similar decomposition temperature for LLDPE/wax blends containing different crosslink densities. [21] Zong et al. found that the silane crosslinked LLDPE samples were more stable than the uncrosslinked LLDPE. [22] The thermal stability of the crosslinked polymer was enhanced with increasing gel content. By contrast, Khonakdar et al. reported that the thermal stability of the HDPE was independent of the crosslinking. [23]

Thermally stable materials are generally achieved by crosslinking. These materials do not undergo melt flow even heated above the crystalline melting temperature. However, one of the drawbacks of crosslinking is a reduction in polymer crystallinity and heat of fusion. [7, 13] In some applications such as insulation for heat exchanger unit, a material with high thermal-energy storage capacity is needed. To investigate the effect of crosslink on energy storage ability of polymer, the retention of ΔH_f (or % ΔH_f retained) of polymer after crosslinking reaction is determined using the following equation.

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

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

For peroxide crosslinked polymers, significant drop in ΔH_f [8, 23-25] and % ΔH_f retained [8, 26] was reported. This was due to the fact that peroxide-crosslinking is performed above the melting temperature of the polymer crystallites. Crosslinks play the role of defect centres which impede the folding of polymer chains, resulting in a decrease in the sizes of the lamellar crystals. [25] In this study, silane-crosslinking causes very slight disturbance on the crystallisation of LDPE and 50/50 blend samples, the values of % ΔH_f retained of 92 and 95 were observed in those samples, respectively. In the case of crosslinked EOR, 90/10, and 70/30 blends, no loss in crystallinity due to crosslinking was observed. Those samples show 100 % ΔH_f retained. Therefore, it could be said that all silane-crosslinked samples investigated in this study have their strong potential to be used for thermal-energy storage applications.

Thermal ageing properties

In this study, the tensile behaviours of all silane-crosslinked blends before and after conducting an ageing test at 110 °C were characterised. It needs to be mentioned here that under this ageing experiment, all of the uncrosslinked blends fail to withstand the heat. This is as expected since the ageing temperature used is higher than the melting temperature of the EOR/LDPE blends. The uncrosslinked samples deform and flow upon heating in a hot-air oven for a short period of time. Apparently, only the crosslinked materials can withstand such a high temperature environment. Figure 7 shows the results of tensile property after thermal ageing experiment. The reduction in tensile modulus and strength was observed after thermal ageing. Such a reduction is more obvious in LDPE than in EOR even though the ageing temperature used in the study (110 °C) is twenty degree higher than the T_m of EOR (87 °C) The silane-crosslinked blends with higher EOR concentrations exhibit better ability to retain their properties after ageing test than those with lower EOR concentrations. This points out that the degree of crosslinking plays significant role in controlling the high temperature properties of polymer.

Conclusions

Various silane-water crosslinked EOR/LDPE blends were prepared under the conditions where self-crosslinking of EOR and LDPE induced by peroxide during reactive extrusion could be negligible. The crosslinked products were characterised for their thermal properties using several techniques including FTIR, DSC, TGA, tensile and ageing test. The degree of crosslinking, as determined by the content of gel, increased with increasing the crosslinking time. The crosslinking degree and rate was found to depend strongly on the amount of crystalline and amorphous portions in the blends. DSC results reveal that recrystallisation of some chains occurs simultaneously during conducting the crosslink reaction. The silane-crosslinked products exhibit good thermal stability and energy storage ability. After ageing test, all uncrosslinked materials fail to withstand the ageing heat. This is unlike to the crosslinked samples. The extent of crosslinking is found to play a major role in the high temperature properties of polymer.

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Figure Captions

Figure 1	Silane-water crosslinking reaction
Figure 2	FTIR spectra of unmodified EOR and silane-grafted EOR
Figure 3	Gel content as a function of immersing time for EOR/LDPE blends
Figure 4	Relationship between gel content and crystallinity in various crosslinked blends
Figure 5a	DSC heating thermograms of various EOR/LDPE blends
Figure 5b	DSC cooling thermograms of various EOR/LDPE blends
Figure 6a	DSC heating thermograms of unmodified EOR, annealed EOR, and crosslinked EOR samples
Figure 6b	DSC heating thermograms of EOR/LDPE (70/30) blend, its annealed sample, and crosslinked sample
Figure 7	Tensile properties of crosslinked blends before and after thermal-ageing test (a) modulus, and (b) tensile strength

Table 1 Melting temperature (T_m), enthalpy of fusion (ΔH_f), crystallisation temperature (T_c), and onset temperature of crystallisation ($T_{c\ onset}$) of unmodified and various grafted EOR/LDPE blends

System	LDPE (%)	Grafting index	T_m (°C)	ΔH_f (J.g^{-1})	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	93.6
	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

Table 2 Melting temperature (T_m), enthalpy of fusion (ΔH_f), crystallisation temperature (T_c), onset temperature of crystallisation ($T_{c\ onset}$), decomposition temperature (T_d) and percentage of ΔH_f retained of crosslinked and annealed EOR/LDPE blends after being crosslinked for 120 hrs

System	LDPE (%)	Gel (%)	T_{m1}, T_{m2} (°C)	ΔH_f ($J.g^{-1}$)	T_c (°C)	$T_{c\ onset}$ (°C)	T_d (°C)	% ΔH_f retained
rosslinked 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

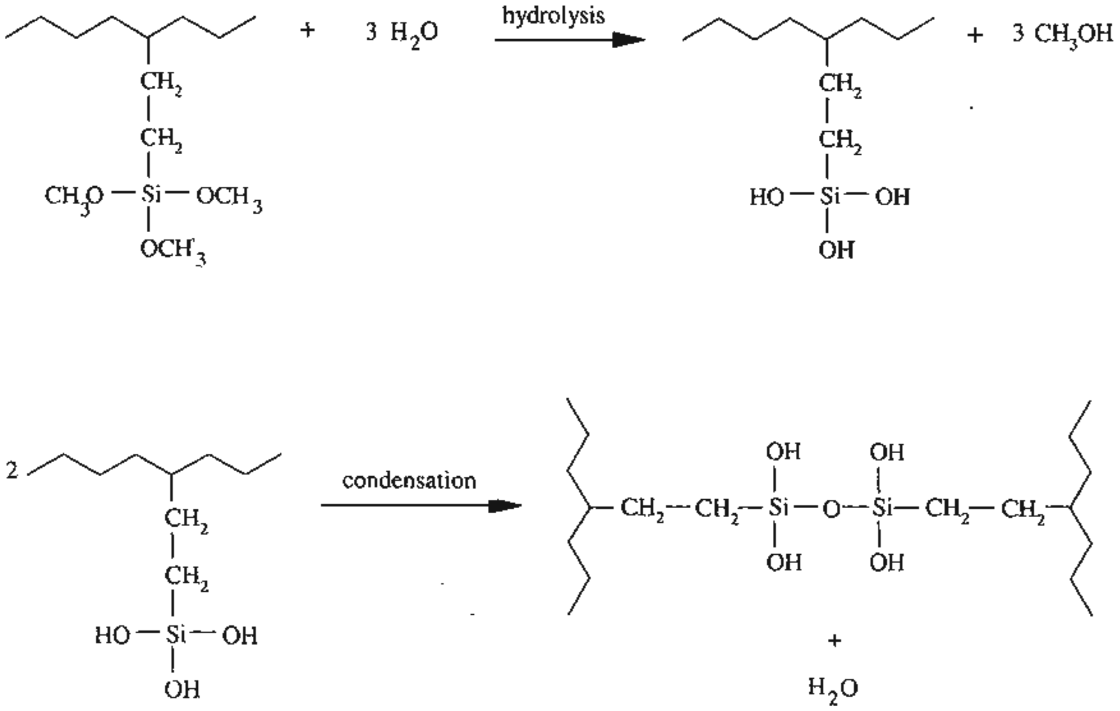
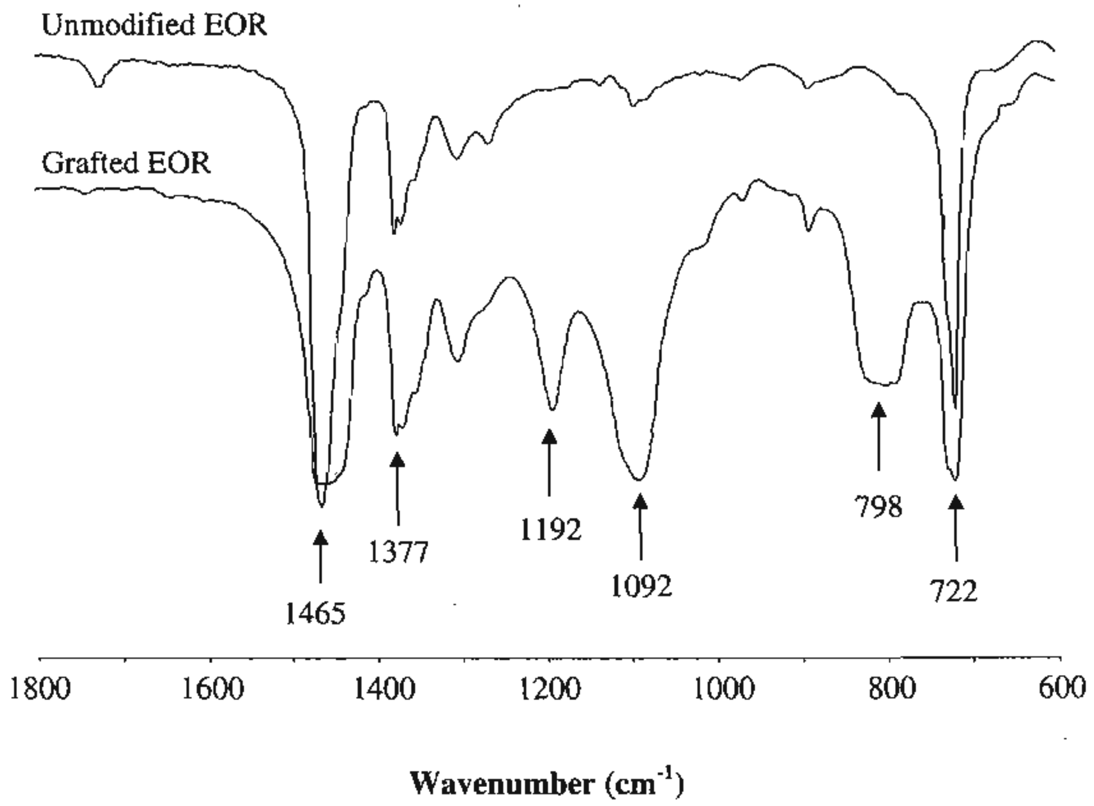


Figure 1 Kalyanee Sirisinha and Sirinya Chimdist



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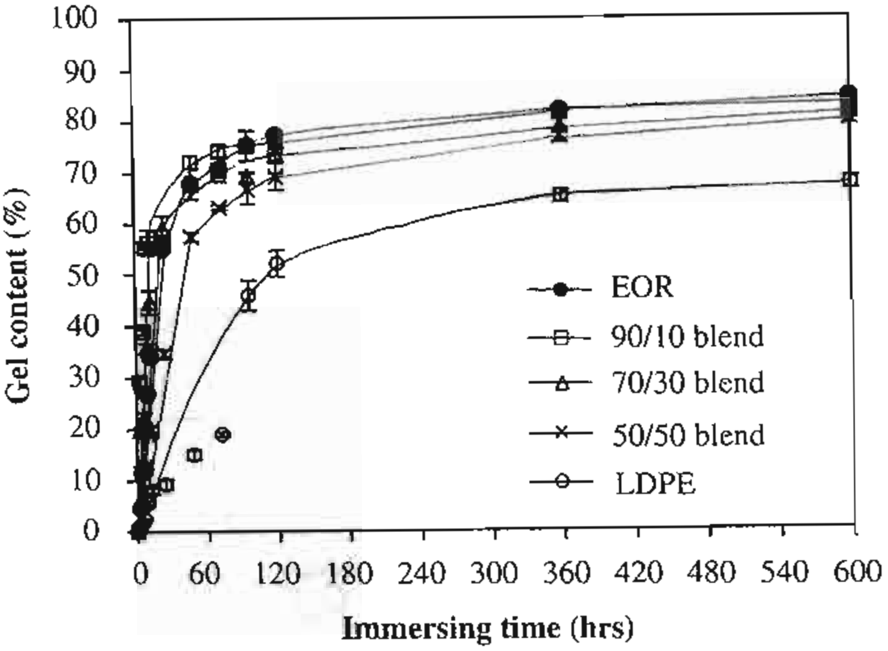


Figure 3 Kalyanee Sirisinha and Sirinya Chimdist

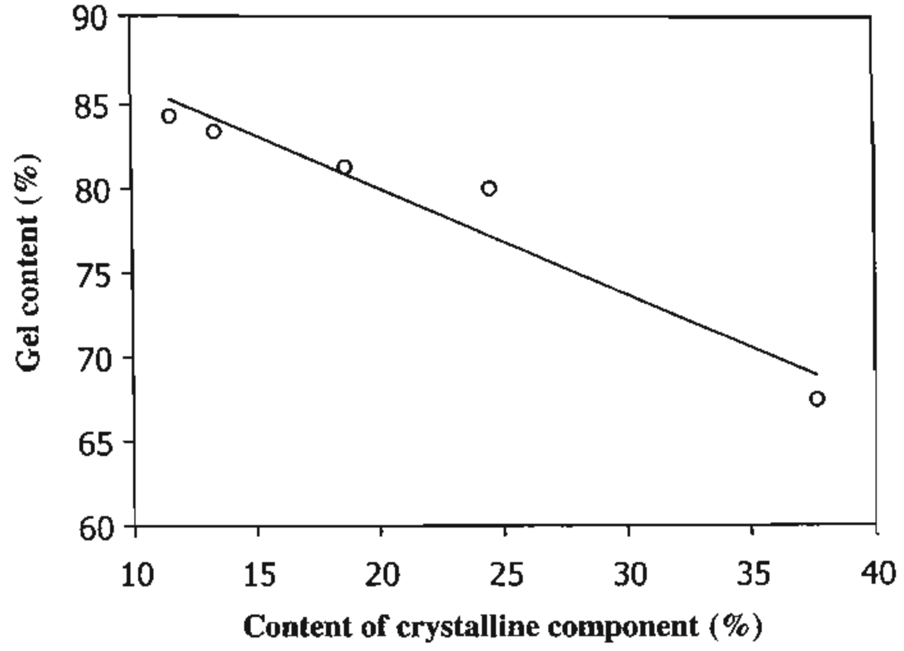
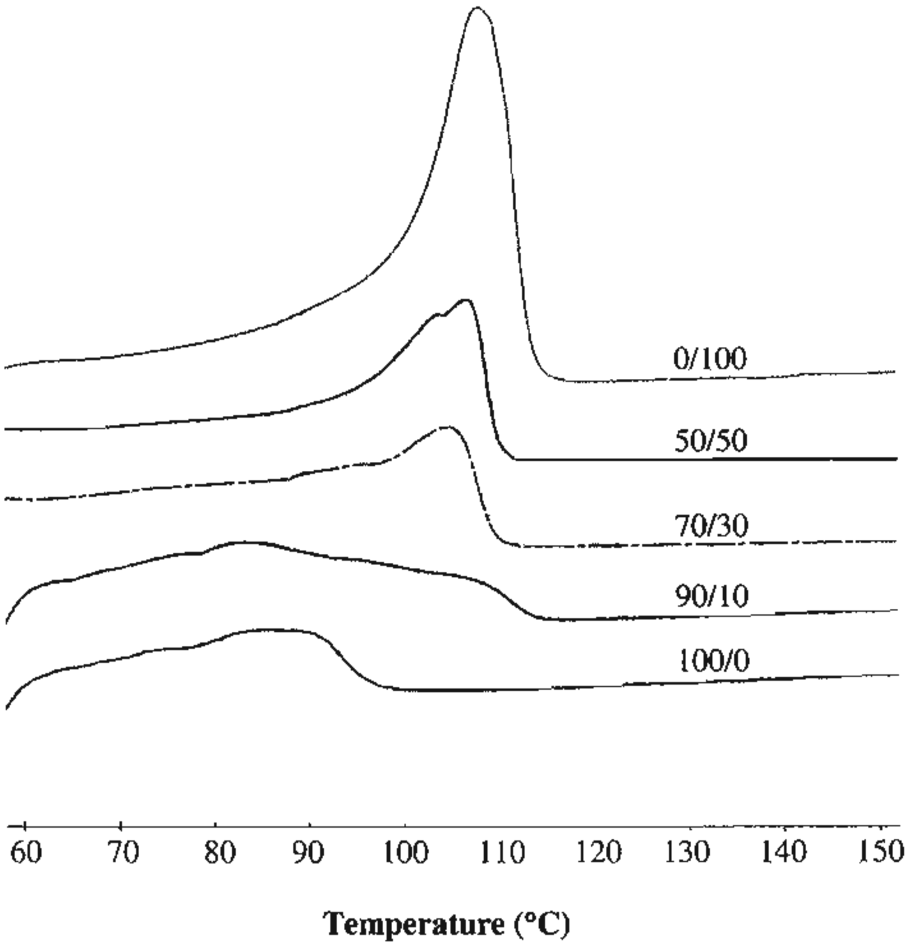


Figure 4 Kalyanee Sirisinha and Sirinya Chimdist



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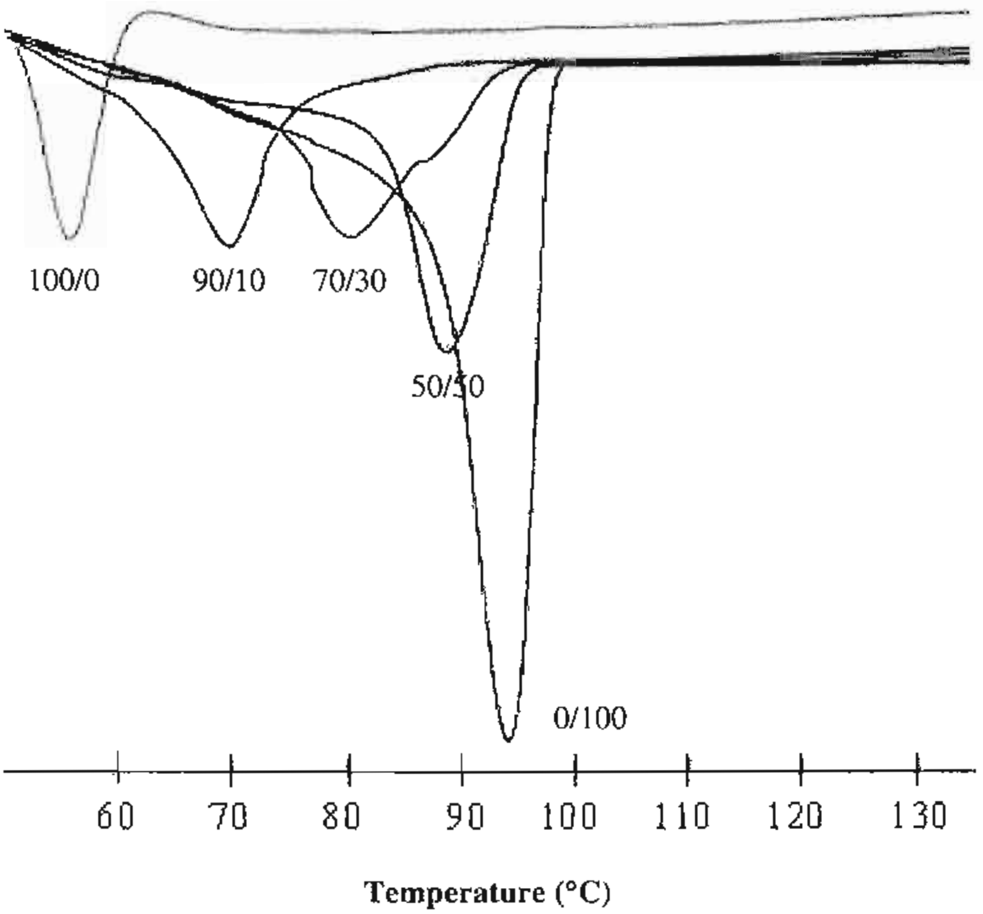

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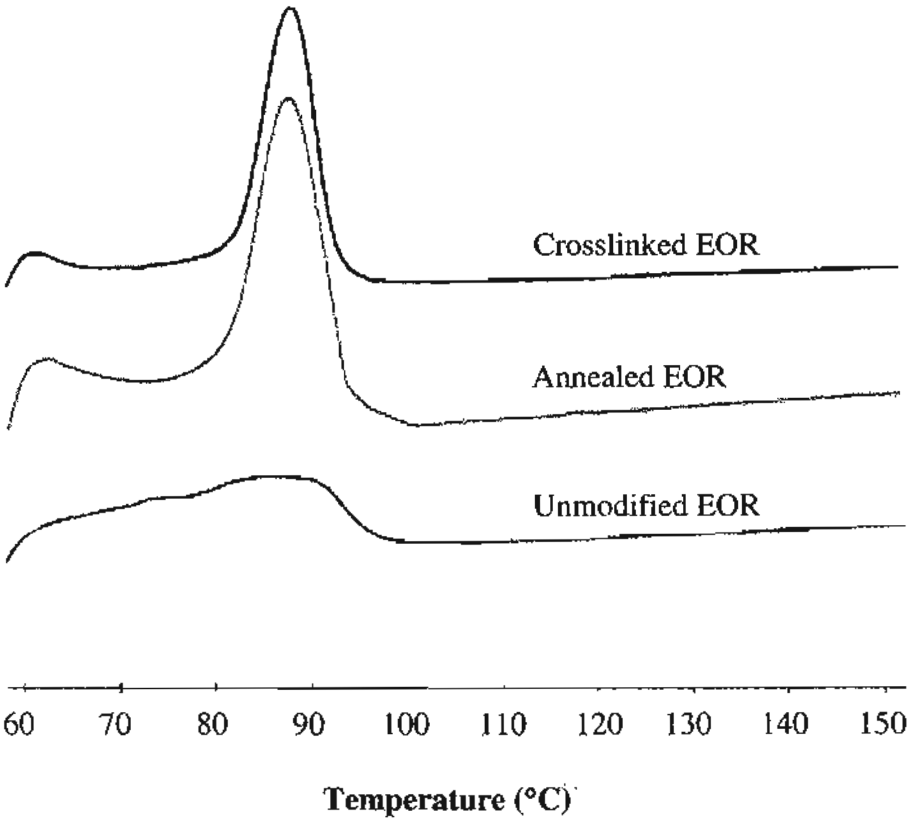

Figure 6a Kalyanee Sirisinha and Sirinya Chimdist

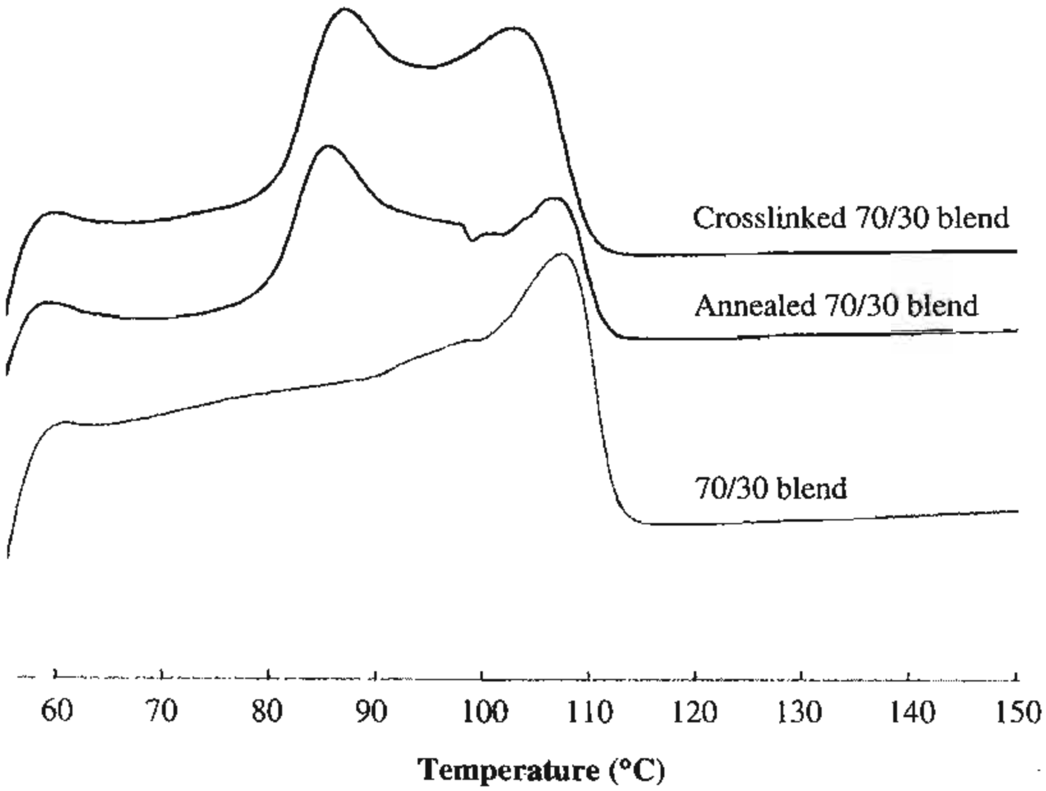

Figure 6b Kalyanee Sirisinha and Sirinya Chimdist

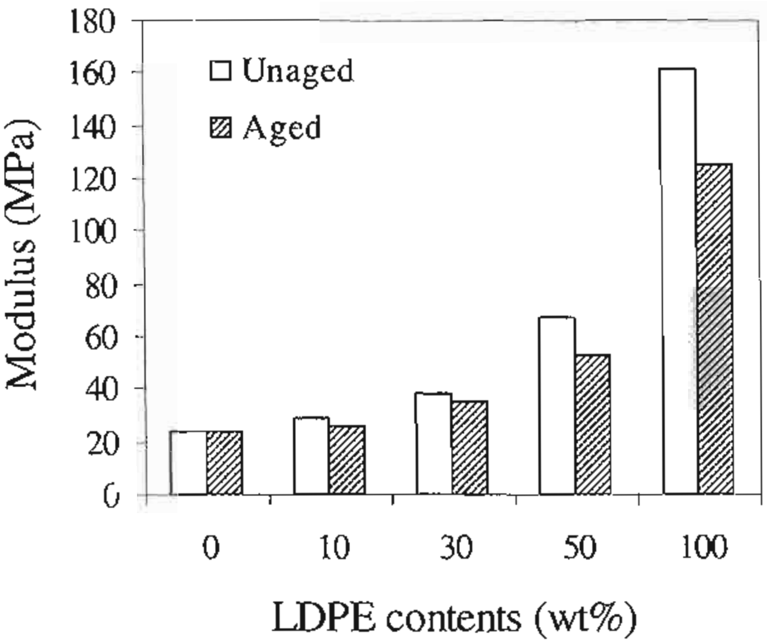

Figure 7a Kalyanee Sirisinha and Sirinya Chimdist

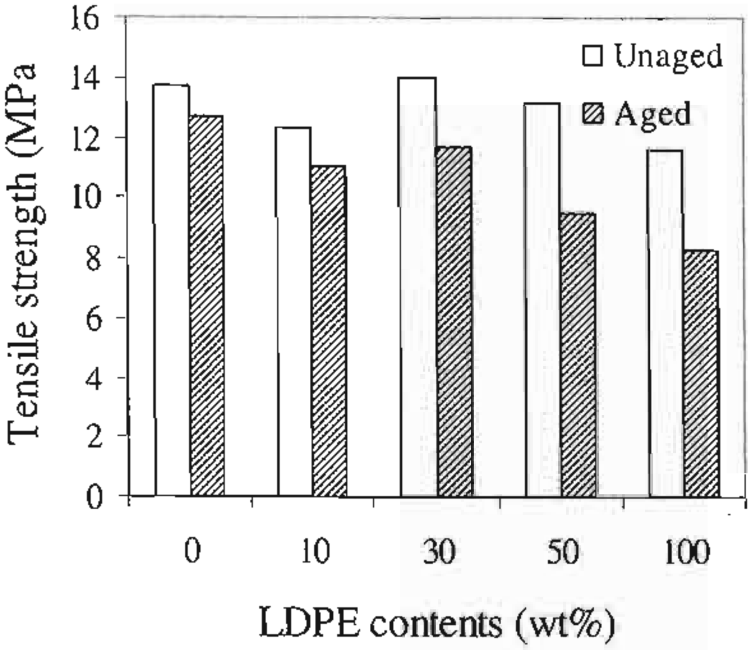

Figure 7b Kalyanee Sirisinha and Sirinya Chimdist

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Title: Progress of silane crosslink reaction of ethylene-octene copolymer as revealed by infrared spectroscopy and rheological measurements

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Abstract: The progress of crosslink reaction of metallocene ethylene-octene copolymer grafted with vinyl trimethoxysilane was studied on a thick specimen. Changes in the concentrations of certain functional groups in different regions as a result of crosslink reaction were followed using attenuated and transmission infrared spectroscopy. The evolution of gel content and crosslink density was analysed for the structure of crosslink formed along the progress of reaction. Infrared results illustrate a heterogeneous crosslink network in the system. The crosslinking process starts with the hydrolysation of methoxy groups in the near-surface layer, proceeding in a diffusion manner. The internal crosslink begins when water molecules are sufficient in the surroundings. A water by-product from the condensation reaction plays an essential part in this centre region. The rheological data and gel results revealed that a tighter network is formed within an existing gel. As the network becomes denser and stronger, the materials act more like elastic and show an improvement in ability for recovery process. However, due to a tight network, water diffusion decreases and immobilization of chain segments disallows conformations necessary for crosslink reaction. As a result, a number of hydrolysable groups and silanol groups are still left for the reaction even after a long crosslinking time.

Progress of silane crosslink reaction of ethylene-octene copolymer as revealed by infrared spectroscopy and rheological measurements

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Abstract

The progress of crosslink reaction of metallocene ethylene-octene copolymer grafted with vinyl trimethoxysilane was studied on a thick specimen. Changes in the concentrations of certain functional groups in different regions as a result of crosslink reaction were followed using attenuated and transmission infrared spectroscopy. The evolution of gel content and crosslink density was analysed for the structure of crosslink formed along the progress of reaction. Infrared results illustrate a heterogeneous crosslink network in the system. The crosslinking process starts with the hydrolysation of methoxy groups in the near-surface layer, proceeding in a diffusion manner. The internal crosslink begins when water molecules are sufficient in the surroundings. A water by-product from the condensation reaction plays an essential part in this centre region. The rheological data and gel results revealed that a tighter network is formed within an existing gel. As the network becomes denser and stronger, the materials act more like elastic and show an improvement in ability for recovery process. However, due to a tight network, water diffusion decreases and immobilization of chain segments disallows conformations necessary for crosslink reaction. As a result, a number of hydrolysable groups and silanol groups are still left for the reaction even after a long crosslinking time.

Keywords: Ethylene-octene copolymer; Crosslinking; Silane

Introduction

Silane-water crosslinking is one of the well-known techniques used in crosslinking polyethylene (PE) [1-9]. It can also be used in the crosslinking of ethylene copolymer [10-14], polypropylene [15-18], polyvinyl chloride [19-20], 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. The crosslink reaction involves hydrolysation and condensation of the hydrolysable groups to form stable siloxane linkages. Since each Si atom has three reactive groups, up to six PE 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% [7]. A similar result was found by Wang et al. [13] 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 extensibity in the crosslinked LDPE containing a high gel content of 90 % [6]. 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 % [10]. 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 progress of silane-water crosslink reaction of EOR and the changes in the formed crosslink structure along the reaction. To achieve this aim, a 6 mm thick sample of silane-grafted polymer was crosslinked in hot water for a specified time in the absence of catalyst. The sample was then sectioned into equally 5 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 analysed together with the evolutions of gel content determined from the standard ASTM D2765-01 and crosslink density obtained from the rheological measurements.

Experimental

Materials

Metallocene ethylene-octene copolymer; EOR (Engage E8003) with a MFI of 1.0 g.10 min^{-1}, was purchased from DuPont Dow Elastomer Co., Ltd. (Wilmington, USA). The peroxide and silane used were dicumyl peroxide (DCP) and vinyl trimethoxysilane (VTMS), respectively. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, Switzerland) and used without purification.

Crosslinking of EOR

The silane-grafting reaction of EOR was carried out in molten state using a co-rotating 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 rev. min^{-1} with a temperature profile of 160, 200, 170, 170 and 170 °C from feed zone to die zone were 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-moulded into 6 mm thick sheets. The moulding temperature used was 190 °C. To conduct a water-crosslink reaction, the moulded sheets were immersed in hot water at 70 °C for a specified time. The samples were then sectioned into equally 5 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 analyse 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 600-4,000 cm^{-1} with a resolution of 4 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 hr. After extraction, the samples were weighed after being dried in a vacuum oven at 55 °C until constant weight. The gel content was calculated using the following equation.

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

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 behaviours were examined at 200 °C under the frequency ranged from 1 to 200 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 hold constant at a given frequency and test temperature. The resultant strain deformation was 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 characterised to determine their gel content and crosslink density. *Fig. 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 hr. The increase in gel content with time is generally observed in various crosslinked systems [7-9, 15].The rate of crosslink reaction, as determined from the slope of the graph, is faster in this early stage of crosslinking. Without catalyst, the EOR reaches 80% gel after 96 hrs. of crosslinking time. Increasing the time further, the gel contents tend to level off. Another effective way of characterising crosslink network is by determining crosslink density (v).This method was reported to be successful in determining the crosslink content of LDPE crosslinked by irradiation process [21]. Based on the theory of elasticity, the number of crosslink in a unit volume or crosslink density can be predicted using the following equation.

$$G^* = vRT \qquad (2)$$

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

The calculated crosslink density of EOR at 20 rad. s^{-1} is shown in *Fig. 2*, where a systematic increase in crosslink density with increasing time is clearly illustrated. 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 paper.

Progress of crosslink reaction

The crosslinking of semicrystalline polymer in the solid state is quite a complex process. As mentioned in the Introduction, crosslinking of the silane-grafted polymers proceeds through the two main reactions as shown in *Fig. 3*. The first reaction begins with the hydrolysation of methoxysilane (Si-OCH$_3$) 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_2O) as a by-product. In this study, it is of interest to find out whether this H_2O 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 5 layers as shown in *Fig. 4*, each layer was analysed 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 hydrolysation and condensation reactions are expected to proceed more rapidly in these two layers, compared to those in layer 3 which is in the centre. In addition, layer 1 and 5 are expected to have similar behaviours. This expectation also goes to layer 2 and 4.

Fig. 5 illustrates examples of FTIR spectrums of crosslinked EOR and Table 1 summarises the absorption frequencies generally used to follow the crosslink reaction. From the TS-FTIR spectra, the presence of Si-OCH$_3$ peak (at 1092 cm^{-1}) is very clear and its evaluation is quite straightforward in which a decrease in its peak intensity clearly reveals a progression in hydrolysation of structure I. In contrast, the situation is more complicated for the two others (Si-OH, and Si-O-Si). The absorption of Si-O-Si (at 1030 cm^{-1}) appears as a shoulder on the larger band of Si-OCH$_3$, this makes difficulties in quantitative measurements of intensity of the Si-O-Si band. Therefore, only the results on the changes in Si-OCH$_3$ groups at 1092 cm^{-1} were followed by TS-FTIR whereas the changes in Si-OH intensities are based on the measurements from ATR mode. 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^{-1}, which was used as the internal reference in the normalisation 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 *Fig.6a and 6b* where the absorption index of Si-OCH$_3$ group (at 1092 cm^{-1}) and Si-OH group (at 3500 cm^{-1}) are plotted against the time of crosslink reaction, respectively. In *Fig. 6a*, 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 behaviour between layer 1 and 5, and between layer 2 and 4 as mentioned earlier. The absorption index of Si-OCH$_3$ peak in all layers does not seem to change after 12 hr 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 hr. With increasing the time of reaction further, a gradual decrease in Si-OCH$_3$ 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 [22].

At 96 hr of crosslinking time, a drastic decrease in the absorption values of the Si-OCH_3 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 hydrolysation of Si-OCH_3 to form Si-OH has taken place in these two layers (1 and 2). However, when analysing the data of Si-OH index in *Fig. 6b*, no increment or any changes in peak intensities of Si-OH could be detected at this stage (96 hr of crosslinking time), illustrating that no Si-OH structure exists in the samples. This points out that after the hydrolysation of Si-OCH_3 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_3 absorption as shown in *Fig. 6a* does not seem to change much even after conducting a reaction for 96 hr. One possible explanation could be the lack of water to aid hydrolysation in the surroundings. The reduction in Si-OCH_3 intensities in the centre region of the specimen becomes more drastic than the other layers when increasing the crosslinking time to 240 hr. It seems obvious that the hydrolysation in this centre region is not controlled only by the amount of water diffused from the outside. At this stage, the absorption index of Si-OH also reaches maximum values. In the other words, there are now a large number of silanols in the samples which are available for the condensation reaction. The presence of Si-OH peak is found also even after 1200 hrs of crosslinking time, revealing that some hydrolysed 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_3 still exists after a long reaction time ($t > 1200$ hr).

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 hydrolysation. Therefore, any factors promoting water diffusion will increase the reaction. With semi-crystalline polymers, the crystalline regions are less accessible to water which must diffuse in to be effective. The hydrolysation 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 [9]. 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 [8]. In addition, hydrolysation leads to the formation of hydrophilic chemical species, i.e. methanol in this case. This makes them accessible to water. Once the Si-OCH_3 groups in the surface and near-surface layers have been hydrolysed, they condense and form Si-O-Si linkage promptly and bleach out water as a by-product. This mechanism undergoes in the near-surface layers for a period of time and thereafter, the reaction in the centre 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_3 intensities in the centre region. By this period of time, the material should be characterised by a large number of crosslink networks. As a result, we observed an increase in gel content (*Fig.1*) and crosslink density (*Fig. 2*) in the crosslinked samples. Increasing the crosslinking time further, (e.g. t > 240 hr) the hydrolysation and condensation reactions 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 be formed 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. Due to 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 immobilises 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 hydrolysable groups left for the crosslink reaction.

Creep behaviours of crosslinked EOR

To further elucidate the effect of crosslink structure on polymer behaviours, rheological experiments using a parallel plate rheometer were performed. *Fig. 7* shows 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. The characteristics of much denser network along the progress of crosslink reaction are clearly revealed.

Fig. 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 behaviour. 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 *Fig. 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.

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 hydrolysation 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, a tighter network is formed within an existing gel. As a consequence, water diffusion decreases and immobilisation of chain segments disallows conformations necessary for crosslink reaction. There are a number of hydrolysable groups and silanol groups left in the samples for further reaction. As the network becomes denser, improvements in material strength and ability for recovery process are resulted.

Acknowledgements

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Table 1 Absorption frequencies used in following silane crosslink reaction

Chemical Structure	Wave number (cm^{-1})
$Si\text{-}OCH_3$	1092
Si-OH	3500
Si-O-Si	1030
C=O	1700

Figure captions

Fig. 1 Evolution of gel content as a function of crosslinking time

Fig. 2 Crosslink density as a function of crosslinking time

Fig. 3 Silane-water crosslink reaction

Fig. 4 Thick specimen used in this study

Fig. 5 FTIR spectrums of silane-grafted EOR and crosslinked EOR

Fig. 6 Absorption index of Si-OCH_3 group at 1092 cm^{-1} (a), and Si-OH group at 3500 cm^{-1} (b) in different layers as a function of crosslinking time

Fig. 7 Comparison of storage modulus (G') among various crosslinked samples (Right and left of Y axis represent the crosslinked sample for $t \leq 96$ and $t > 96$ hrs, respectively.)

Fig. 8 Comparison of creep compliance (J) among various crosslinked samples

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

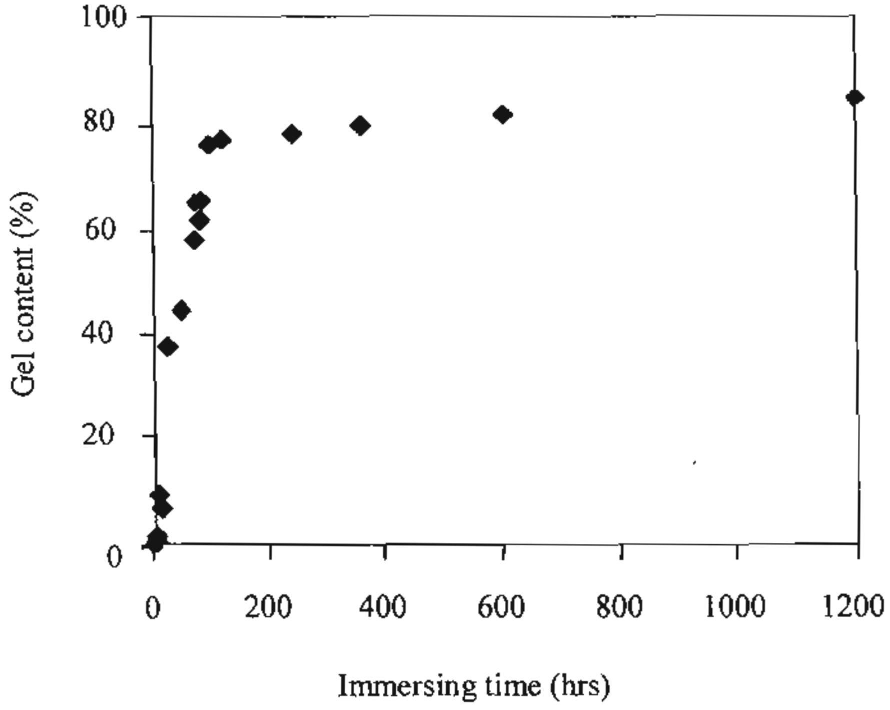
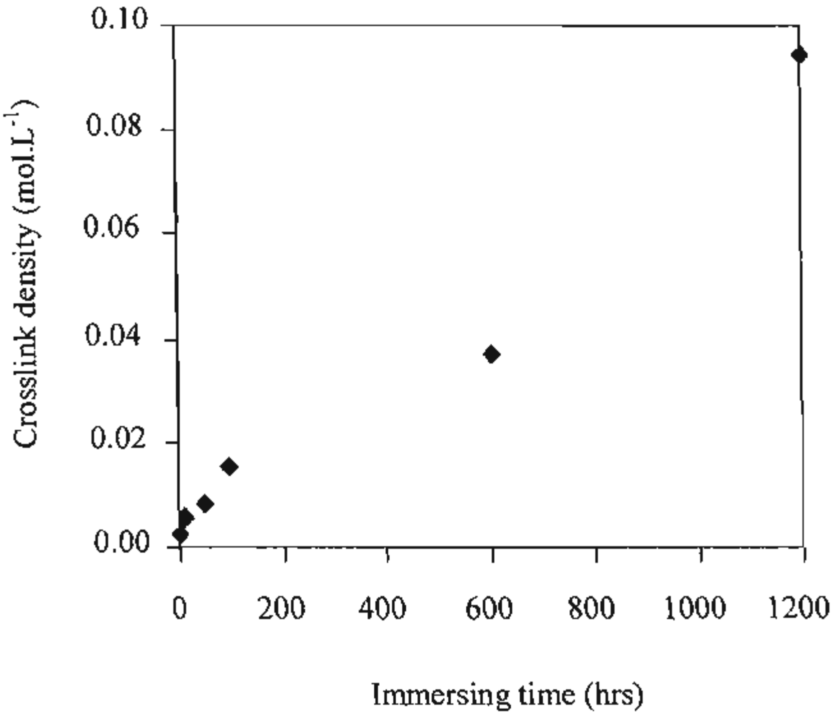


Fig. 1 Kalyanee Sirisinha and Walailuck Kamphunthong



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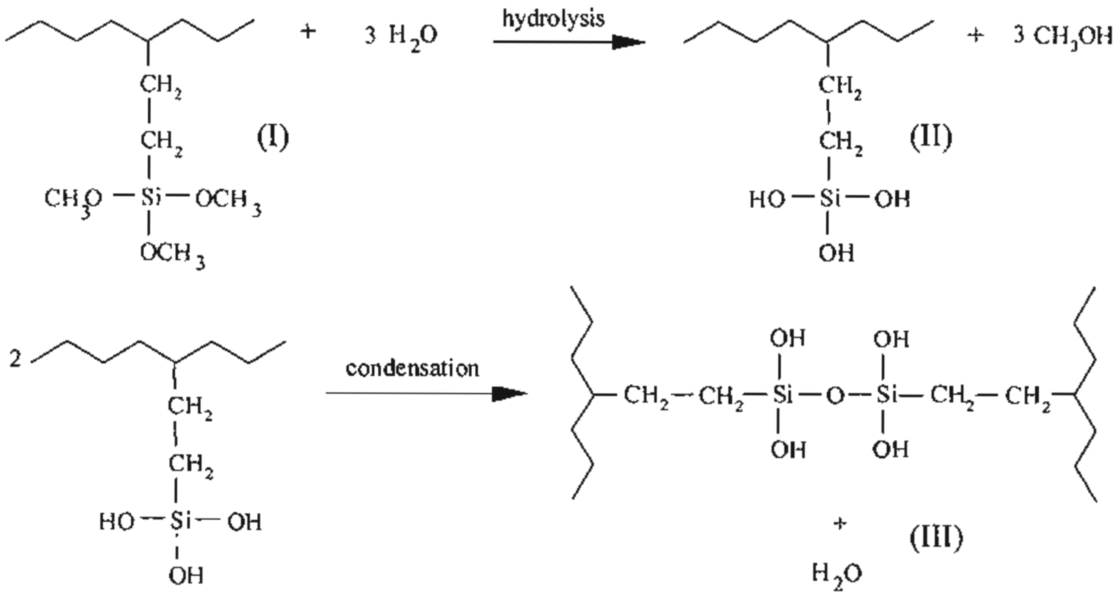
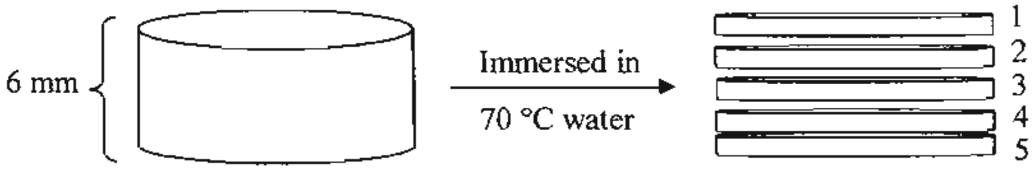


Fig. 3 Kalyanee Sirisinha and Walailuck Kamphunthong



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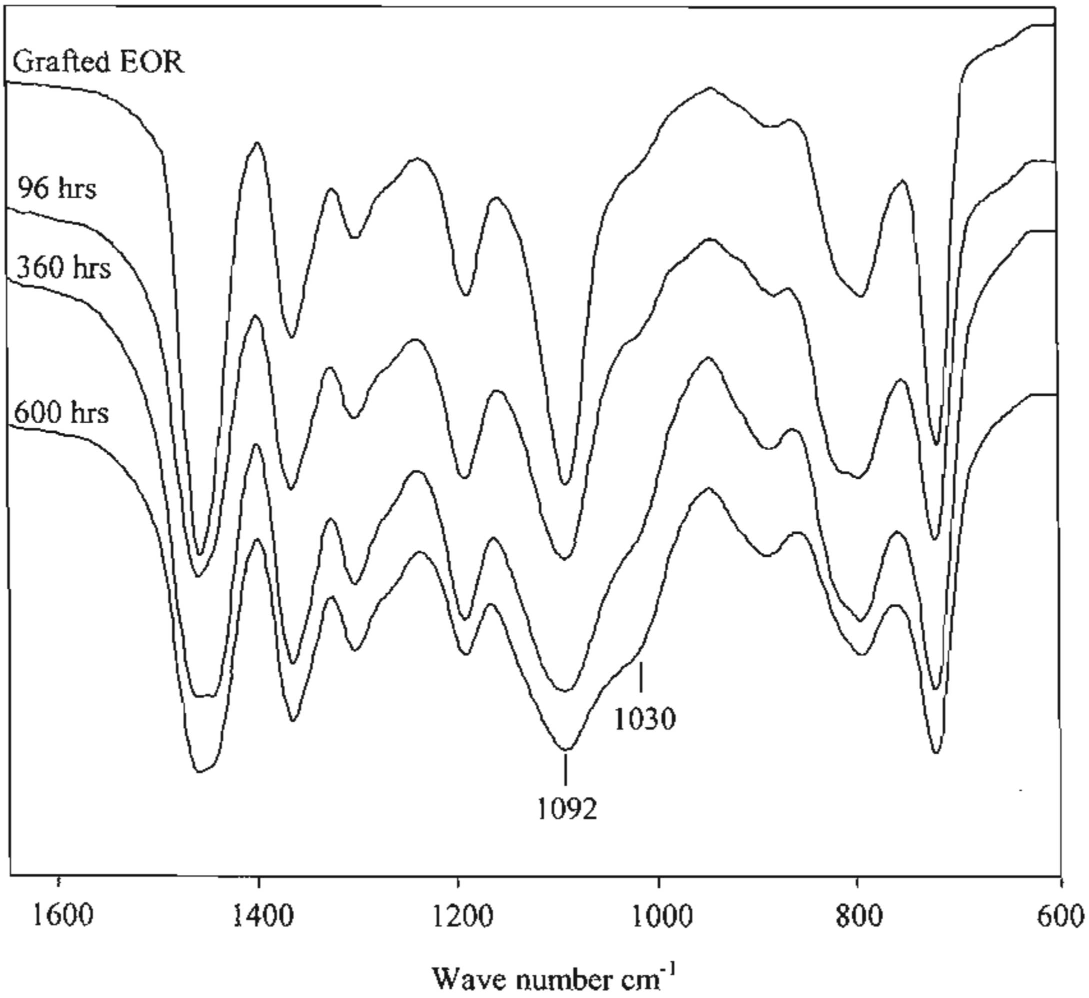

Fig. 5 Kalyanee Sirisinha and Walailuck Kamphunthong

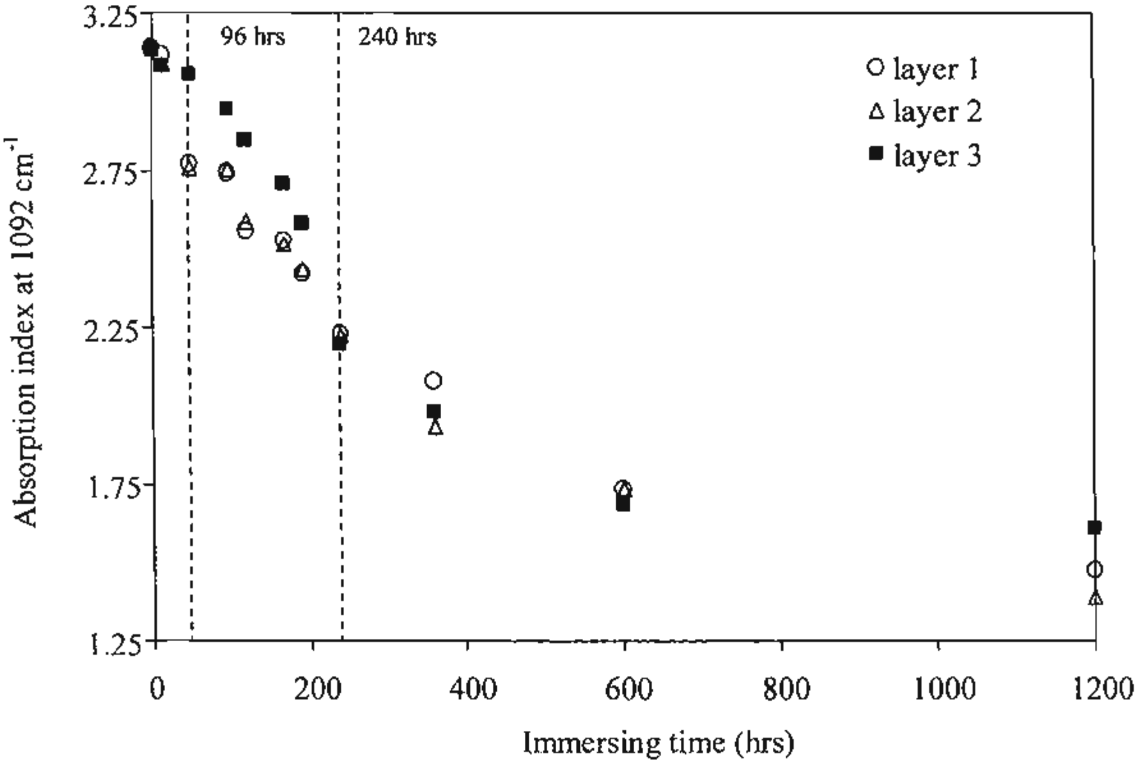

Fig. 6a Kalyanee Sirisinha and Walailuck Kamphunthong

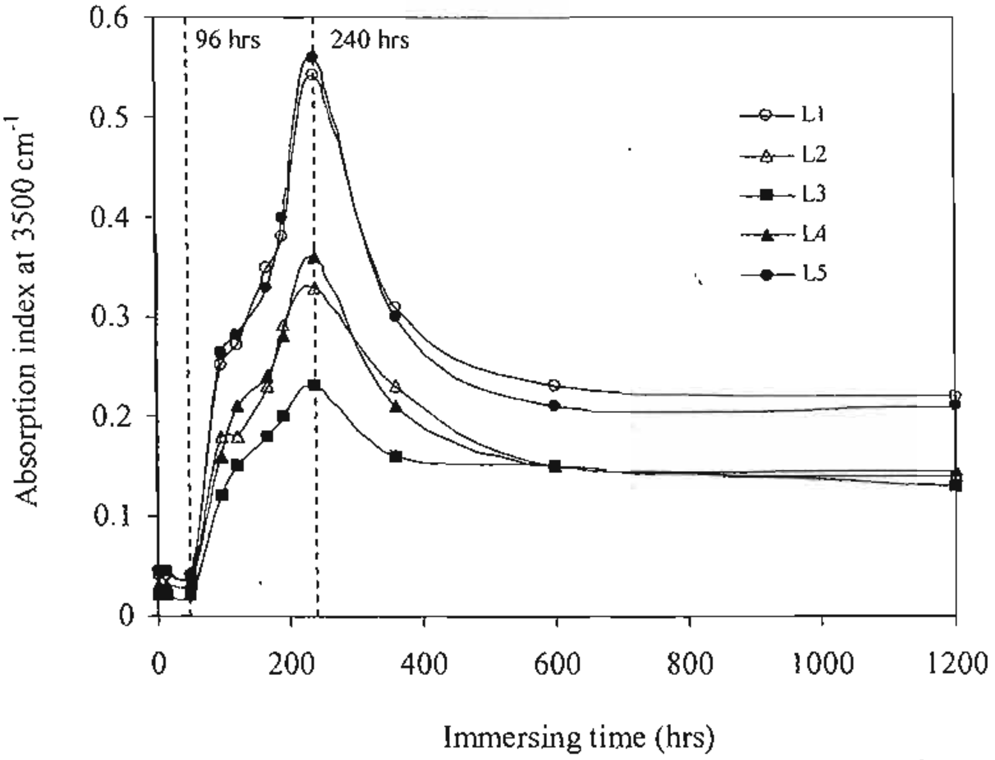

Fig. 6b Kalyanee Sirisinha and Walailuck Kamphunthong

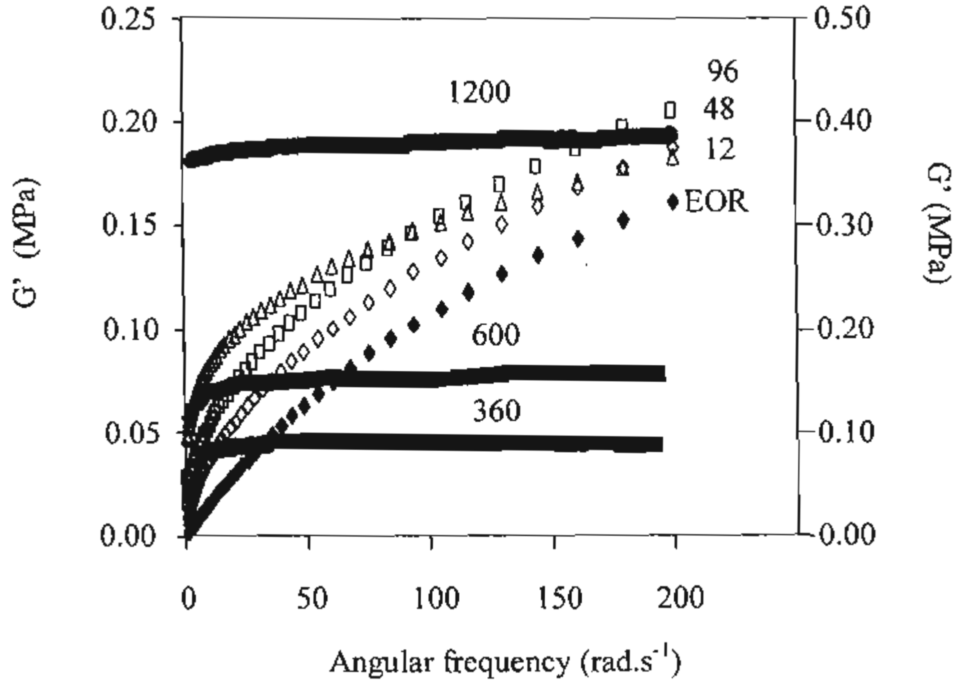

Fig.7 Kalyanee Sirisinha and Walailuck Kamphunthong

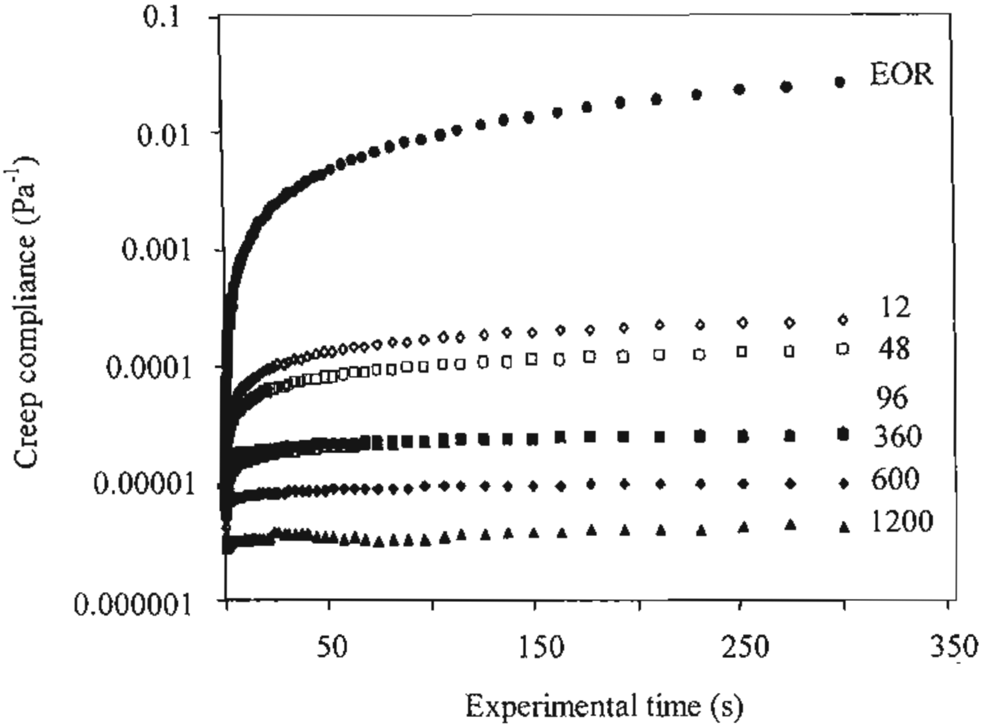

Fig.8 Kalyanee Sirisinha and Walailuck Kamphunthong

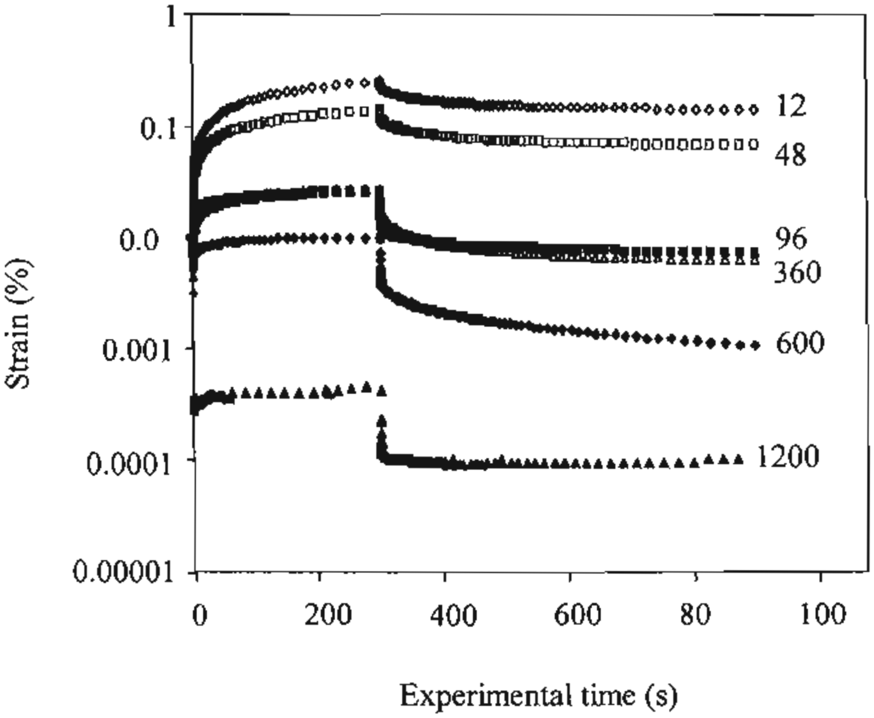

Fig. 9 Kalyanee Sirisinha and Walailuck Kamphunthong

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Characterising method for elucidating crosslinking degree in silane-water crosslinked polymer composites

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Abstract

Crosslinking degree in the silane-water crosslinked ethylene-octene copolymer was investigated, using three different techniques namely the conventional gel content determination, FTIR analysis and rheological measurement. The effects of time and addition of calcium carbonate filler on the crosslinking reaction were also studied. The results show that FTIR analysis and rheological measurement could be used as alternative methods in elucidating crosslinking degree. Those techniques are less time-consuming and are more environmental friendly. The crosslinking time and the presence of filler were found to play important roles in the silane-water crosslinking reaction.

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1. Introduction

Crosslinking is an important method for extending the service temperature of polymer. Crosslinked polymer can be produced in a variety of ways. In recent years the silane-water crosslinking has gained much interest because of favorable properties and ease of processing in the crosslinked product. In such technique, a polymer is grafted with alkoxysilanes and subsequently crosslinked in water by means of hydrolysis and condensation of those units to form siloxane bonds.

Degree of crosslinking is a main factor controlling properties of the crosslinked products. The approach, which is widely used in the determination of crosslinking degree, is based on ASTM 2765-95a. The method involves measuring the content of gel or the insoluble fraction produced in the crosslinked material after extracting with solvents. Even though, the gel content determination is a direct way of elucidating the crosslink content, the experiment consumes amount of time and solvent for extraction. In addition, the test results were found to produce ambiguous meanings on the explanation of crosslinking effect on the product properties[1-3] and on the progress of silane-crosslinking reaction[3].

This paper reports the alternative characterisation methods for elucidating the degree of crosslinking in silane-water crosslinked ethylene-octene copolymer (EOR) and its composites filled with calcium carbonate ($CaCO_3$). Three methods investigated include the gel content determination, infrared analysis and rheological measurement.

2. Experimental

2.1 Materials

Ethylene-octene copolymer (EOR) grade ENGAGE E8003, DuPont Dow Elastomer Co. Ltd. was used. Calcium carbonate (Turboplex, Lime Quality Co. Ltd., Bangkok, Thailand) used was surface-coated with 2 wt-% stearic acid. For grafting reaction, the initiator was dicumyl peroxide (DCP) and the silane used was vinyltrimethoxysilane (VTMS).

2.2 Preparation of EOR composites

The EOR and $CaCO_3$ masterbatch was compounded in the ratio of 80/20 wt-% through an intermeshing co-rotating twin-screw extruder. The operated temperature profile was in the range of 160-200°C. A screw speed was controlled at 150 rpm.

2.3 Preparation of silane-water crosslinked materials

The silane-grafting reaction of either unfilled or $CaCO_3$ filled EOR with 5wt-%VTMS and 0.1wt-%DCP was carried out in a twin-screw extruder. The temperatures were carefully controlled in the range of 160-200°C, with a screw speed of 30 rpm. The grafted products were, then, immersed in hot water at 70°C to conduct a crosslink reaction. The effect of time for the reaction was investigated. In this study, no catalyst was used for accelerating the crosslink reaction.

2.4 Characterisation

Gel content determination

The gel content was determined according to ASTM D2765-95a. The sample was wrapped in a 120-mesh stainless steel cage and extracted in boiled xylene for 6 h. After extraction, the cage was dried in a vacuum oven, the gel content being defined as follows.

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

FTIR analysis

FTIR was used to analyse the presence of silane in the grafted products and to determine the crosslinking degree by means of analysing the changes in contents of methoxy- and siloxane-groups. Films with 100μm thickness were prepared by hot pressing at 200°C. Before the measurement, the films were washed with an excess amount of acetone to remove ungrafted silane or peroxide. The IR spectra were recorded using Equinox 55 FTIR spectrometer.

Rheological measurement

A dynamic rheometer (Physica MCR 500) with 25 m diameter parallel plate was used in an oscillatory she mode. The rheological behaviours of the crosslink products were examined at 200°C.

3. Results and discussion

Figure 1 shows the relationship between the content gel and the time of crosslinking. It is clearly seen th the gel develops in the initial stage of crosslinking tir and its content sharply increases with increasing tin The gel content of 80 % is observed after crosslinki time of 84 h. With increasing time beyond 84 h, the g content increases very slightly. For crosslink composites, the similar trend is observed but in a higl magnitude of gel content obtained. This could be caus by a trap of fillers inside the crosslinked network.

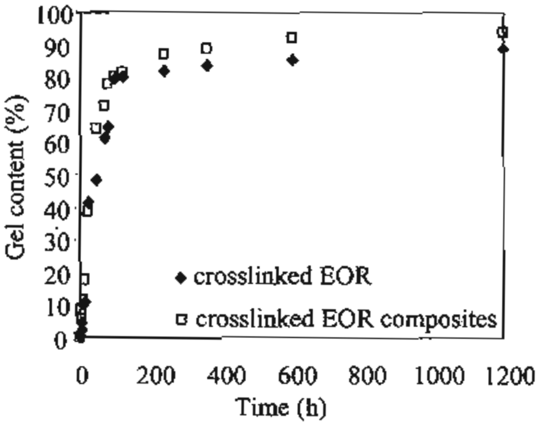

Figure 1. The plot of gel content as a function crosslinking time

Figure 2 represents the plot of IR absorption index crosslinking time. As mentioned earlier, during crosslink reaction, trimethoxysilane groups w hydrolysed and condensed to form siloxane linkag Therefore, an increase in Si-O-Si or a decrease in

Bangkok, Thailand) used was surface-coated with 2 wt-% stearic acid. For grafting reaction, the initiator was dicumyl peroxide (DCP) and the silane used was vinyltrimethoxysilane (VTMS).

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The EOR and $CaCO_3$ masterbatch was compounded in the ratio of 80/20 wt-% through an intermeshing co-rotating twin-screw extruder. The operated temperature profile was in the range of 160-200°C. A screw speed was controlled at 150 rpm.

2.3 Preparation of silane-water crosslinked materials

The silane-grafting reaction of either unfilled or $CaCO_3$ filled EOR with 5wt-%VTMS and 0.1wt-%DCP was carried out in a twin-screw extruder. The temperatures were carefully controlled in the range of 160-200°C, with a screw speed of 30 rpm. The grafted products were, then, immersed in hot water at 70°C to conduct a crosslink reaction. The effect of time for the reaction was investigated. In this study, no catalyst was used for accelerating the crosslink reaction.

2.4 Characterisation

Gel content determination

The gel content was determined according to ASTM D2765-95a. The sample was wrapped in a 120-mesh stainless steel cage and extracted in boiled xylene for 6 h. After extraction, the cage was dried in a vacuum oven, the gel content being defined as follows.

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

FTIR analysis

FTIR was used to analyse the presence of silane in the grafted products and to determine the crosslinking degree by means of analysing the changes in contents of methoxy- and siloxane-groups. Films with 100μm thickness were prepared by hot pressing at 200°C. Before the measurement, the films were washed with an excess amount of acetone to remove ungrafted silane or residual peroxide. The IR spectra were recorded using an Equinox 55 FTIR spectrometer.

Rheological measurement

A dynamic rheometer (Physica MCR 500) with 25 mm diameter parallel plate was used in an oscillatory shear mode. The rheological behaviours of the crosslinked products were examined at 200°C.

3. Results and discussion

Figure 1 shows the relationship between the content of gel and the time of crosslinking. It is clearly seen that the gel develops in the initial stage of crosslinking time and its content sharply increases with increasing time. The gel content of 80 % is observed after crosslinking time of 84 h. With increasing time beyond 84 h, the gel content increases very slightly. For crosslinked composites, the similar trend is observed but in a higher magnitude of gel content obtained. This could be caused by a trap of fillers inside the crosslinked network.

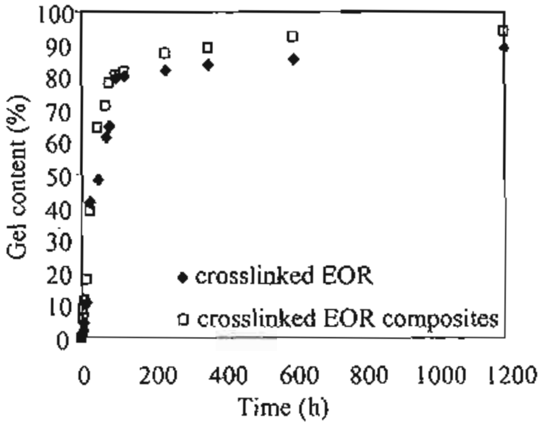

Figure 1. The plot of gel content as a function of crosslinking time

Figure 2 represents the plot of IR absorption index and crosslinking time. As mentioned earlier, during the crosslink reaction, trimethoxysilane groups were hydrolysed and condensed to form siloxane linkages. Therefore, an increase in Si-O-Si or a decrease in Si-

OCH_3 peak intensities would indicate the progress in crosslink reaction. However, it is difficult to determine the intensity of Si-O-Si peak since it presents as a shoulder of the Si-OCH_3. In this study, a decrease in the intensity of Si-OCH_3 band at 1092 cm^{-1} is, thus, followed to express the progress of silane crosslink reaction. The results are reported in the term of absorption index (AI), which is a relative intensity of the Si-OCH_3 peak with the internal reference peak. From figure 2, the AI values slightly decrease with increasing time, indicating an increase in siloxane linkages. Similar trend is observed in the composite system.

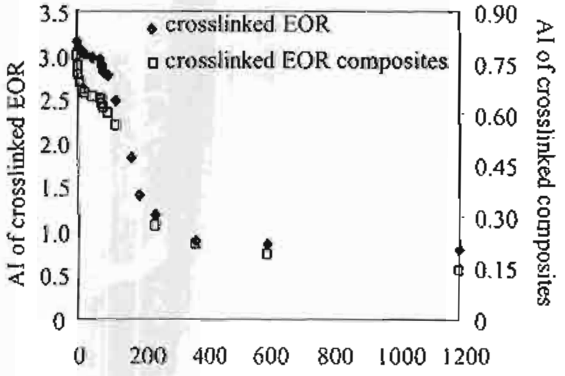

Figure 2. The plot of absorption index (AI) as a function of crosslinking time

Figure 3 demonstrates the plot of complex modulus (G*) of EOR and EOR composites as a function of crosslinking time. According to elastic theory[4], crosslink density directly depends upon G*, thus, an observed increase in G* after a longer crosslinking time can be inferred to an increase in crosslink density. The magnitudes of G* seem higher in the crosslinked composites. This could be due to an obstruction of polymer flow by particulate fillers in such systems.

4. Conclusions

Silane crosslinked EOR and EOR composites were characterised for their degree of crosslinking using three different techniques, namely gel content determination, FTIR analysis and rheological measurement. The results show that not only the gel content determination, which gives a direct result on crosslinking degree, but the FTIR analysis and G* measurement could be used as alternative methods. The latter two techniques also take less time-consuming and more environmental friendly. However, care must be taken in interpretation of results, especially in the case of crosslinked composites containing filler.

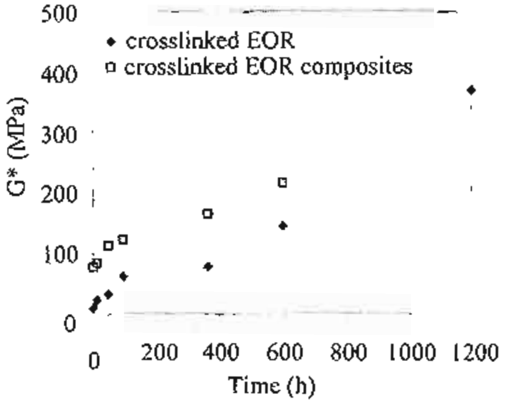

Figure 3. The plot of complex modulus (G*) as a function of crosslinking time

5. Acknowledgement

The Thailand Research Fund and Commission on Higher Education are acknowledged.

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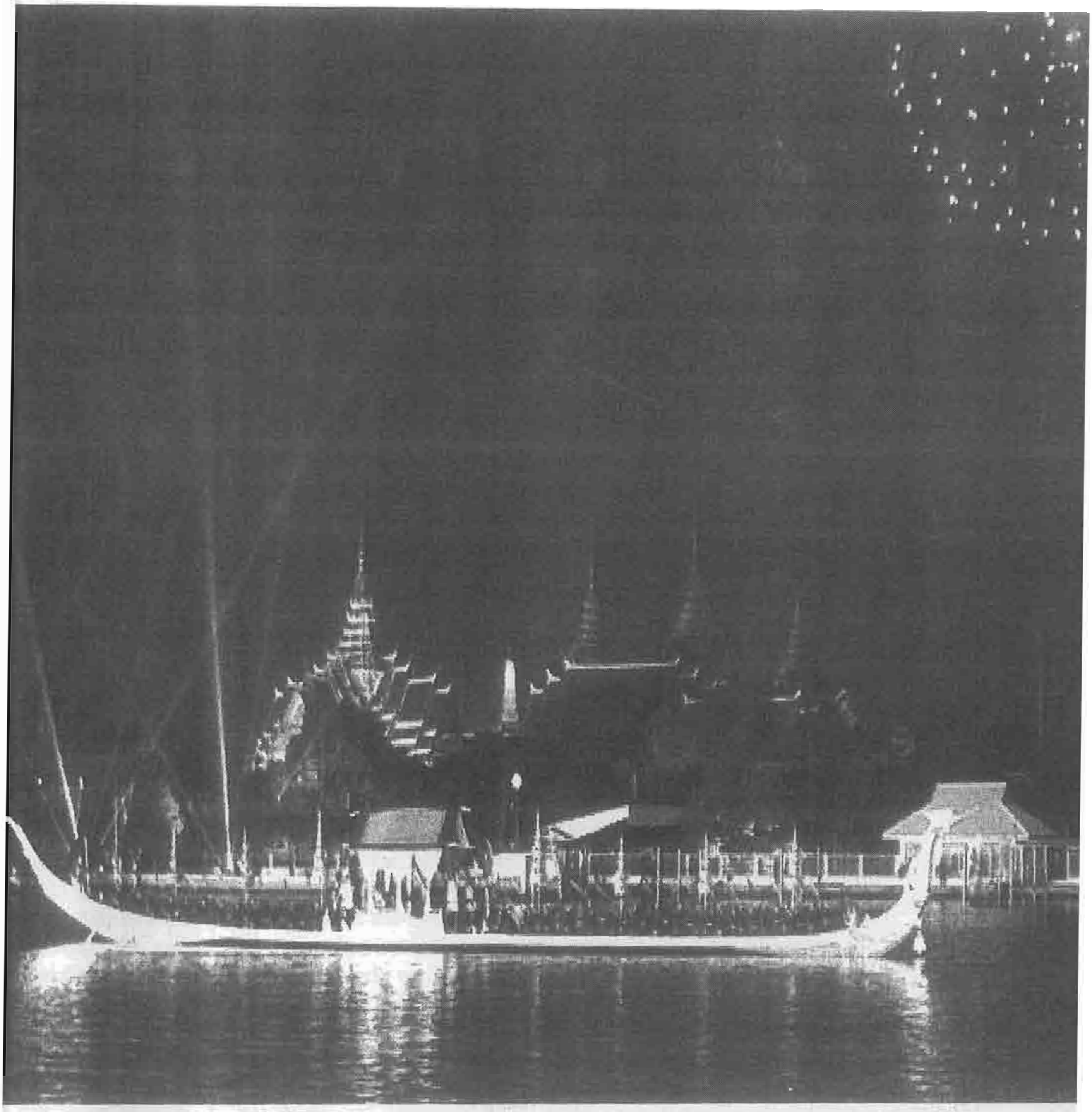

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Changes in rheological properties of elastomeric ethylene copolymer along the progress of silane crosslinking process

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ABSTRACT

Dynamic viscoelastic measurements have been carried out on a series of silane-water crosslinked ethylene-octene copolymer (EOR) to investigate the changes in rheological properties and crosslink structure along the progress of crosslink reaction. Two rheological experiments were performed on a parallel plate rheometer in both frequency sweep and creep-recovery modes. The viscoelastic behaviours of the grafted and crosslinked EORs were governed by elastic response, indicated by the higher values of storage modulus (G') over that of loss modulus (G"). The G' values and % strain recovery were found to increase with increasing crosslinking time. The results of rheological test and gel study pointed out that a number of polymer chains involved in the network structure hardly changed after 96 hrs of crosslinking time but more siloxane linkages occur, leading to a systematic change in viscoelastic properties without a detection of weight change on the gel fraction.

Introduction

Crosslinking is one important method for improving the high temperature properties of polymer. The silane-water crosslinking, unlike to the typical peroxide crosslinking or irradiation crosslinking, introduces the siloxane bonds between polymer chains, instead of carbon-carbon bonds (*Figure 1*). The silane crosslinking process also conducts while the polymer is in the solid-state. Thus the crystallinity of polymer could complicate the crosslink situation. When polymer chains are linked, the content of insoluble material (gel) is one of the basic parameters characterising the structure of material. The gel content determination is thus a widely used method for following the crosslink reaction. In a recent work we reported the gel content results of various silane-water crosslinked systems [1-2]. The results showed ambiguous meanings on the explanation of effect of crosslinking on the product properties [1] and on the progress of silane-water crosslink reaction and crosslink structure after a prolonged crosslinking time [1]. In this paper, we present dynamic viscoelasticity results of a series of elastomeric ethylene-octene copolymers (EOR) of different crosslinking degree. Two rheological experiments are performed, i.e. frequency sweep test and creep-recovery experiment. These experiments can give one insight on the understandings of the progress of silane crosslinking process.

Experimental

Materials

EOR (ENGAGE E8003) with MFI of 1.0 g.10 min^{-1}, was purchased from DuPont Dow Elastomer Co. Ltd. (Wilmington, USA). The peroxide and silane were dicumyl peroxide (DCP) and vinyl trimethoxysilane (VTMS), respectively.

Preparation of crosslinked polymers

The silane-water crosslinking process consists of two steps; i.e. silane-grafting of EOR and crosslinking of the grafted polymer. The grafting reaction of EOR with 5wt-

%VTMS and 0.1wt-%DCP was carried out in a twin-screw extruder. The temperatures were carefully controlled in the range of 160-200°C, with a screw speed of 30 rpm. The grafted products were, then, immersed in hot water at 70°C to conduct a crosslink reaction. No catalyst was used in the crosslinking process.

Rheological measurements

Frequency sweep test - The parallel plate rheometer (Physica MCR 500) was operated in an oscillatory shear mode at a constant strain of 10%. The rheological behaviours were examined at 200 °C under the frequency ranged from 1 to 200 rad.s^{-1}. The resultant storage (G'), loss (G") and complex modulus (G*) values were recorded.
Creep and recovery test - The applied stress was hold constant at a given frequency and test temperature. The resultant strain deformation was 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.

Determination of gel content

The gel content was determined according to ASTM D2765-95a. The sample was wrapped in a 120-mesh stainless steel cage and extracted in boiled xylene for 6 h. After extraction, the cage was dried in a vacuum oven. The gel content was determined from the dried content of insoluble fractions after extraction process with respect to the original sample content.

Results and discussion

Figure 2 shows the plot of G' and G" of the neat EOR and its modified as a function of frequency. A very strong frequency dependence of G' and G" of the neat elastomer indicates the domination of viscous response which is a characteristic of uncrosslinked melt. The introduction of silane units increases irregularity in polymer structure and chain entanglement in the grafted polymers. As a result, the G' values of the grafted sample are somewhat higher than those of neat polymer throughout the entire frequency. After conducting a crosslink reaction, the flattening of G' and G' being higher than G" indicate that the samples in the present experiment were crosslinked from lightly to heavily. The effects of crosslinking time on G' values are clearly seen in *Figure 3*, revealing the characteristics of much denser network along the progress of crosslink reaction. The results of strain recovery experiment reveal also a drastic snapback of strain after stress removal due to the existence of elastic structure inside the crosslinked samples. Increasing the crosslinking time the % strain recovery is observed. These rheological results seem to be more meaningful than those of gel results as shown in *Figure 4*. A systematic increase in gel contents with time is only observed below 96 hrs of crosslinking process where the content of approximately 80% was reached. Increasing the time further, the contents of gel scarcely change. From the rheological results and gel study, it could be said that a number of polymer chains involved in the network structure are hardly changed after 96 hrs of crosslinking time but more siloxane linkages occur, leading to a systematic change in viscoelastic properties without a detection of weight change on the gel fraction. This dictates that the silane crosslinking process is still progressed for a long time after gel content reaches plateau region.

Conclusions

Various silane-water crosslinked EOR were prepared. The G', G" and G* were measured by a parallel plate rheometer in a frequency sweep mode whereas the strain recovery and creep compliance were determined from creep and recovery test. The results revealed the domination of elastic phase and frequency independent behaviour in the silane-crosslinked products. By increasing the time of crosslinking process, the crosslinked structure became denser, leading to a product with improvement in ability for recovery process.

Acknowledgement

The Thailand Research Fund and the Commission on Higher Education.

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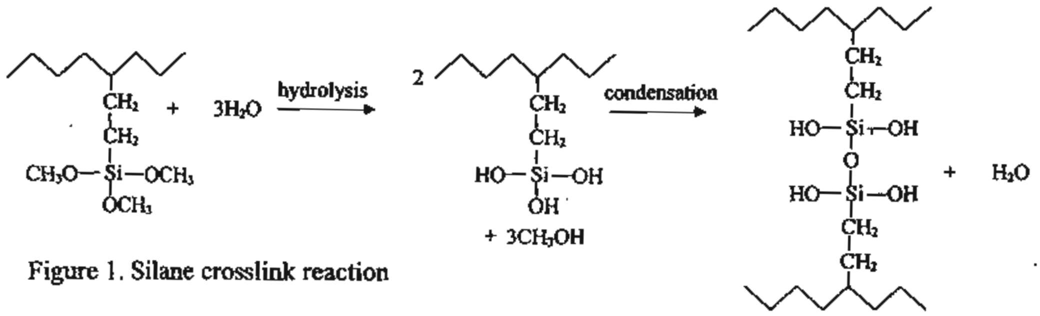

Figure 1. Silane crosslink reaction

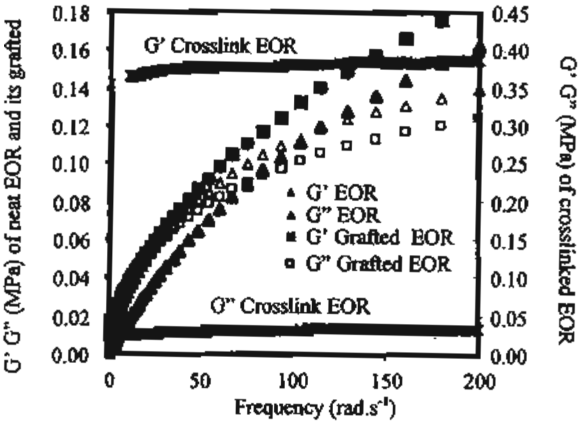

Figure 2. G' and G" of various EORs as a function of frequency

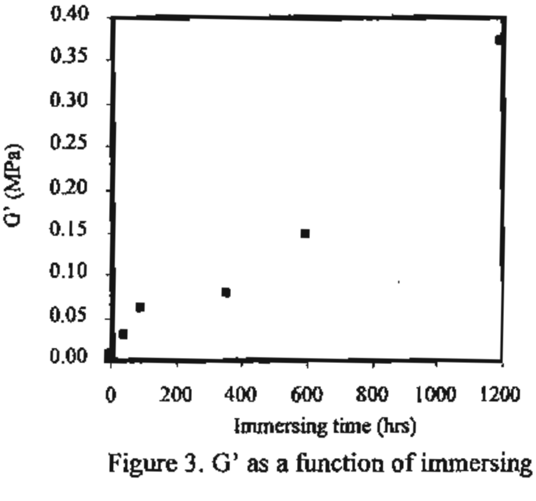

Figure 3. G' as a function of immersing time

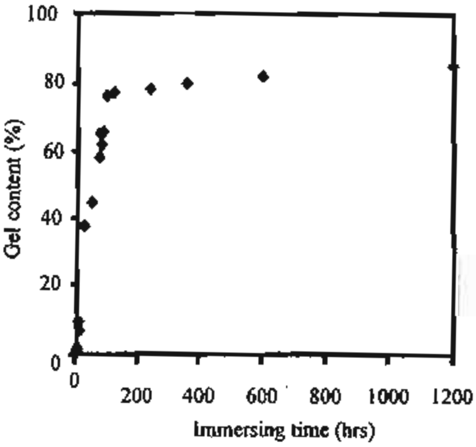

Figure 4. The plot of gel content as a function of time

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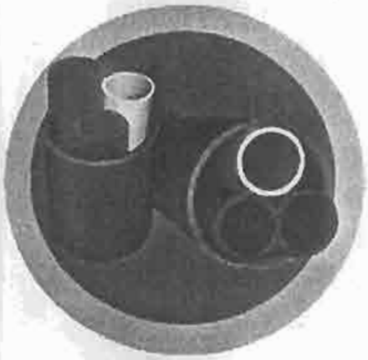

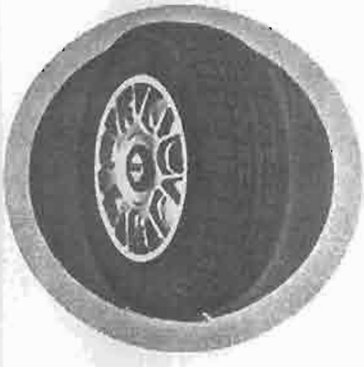

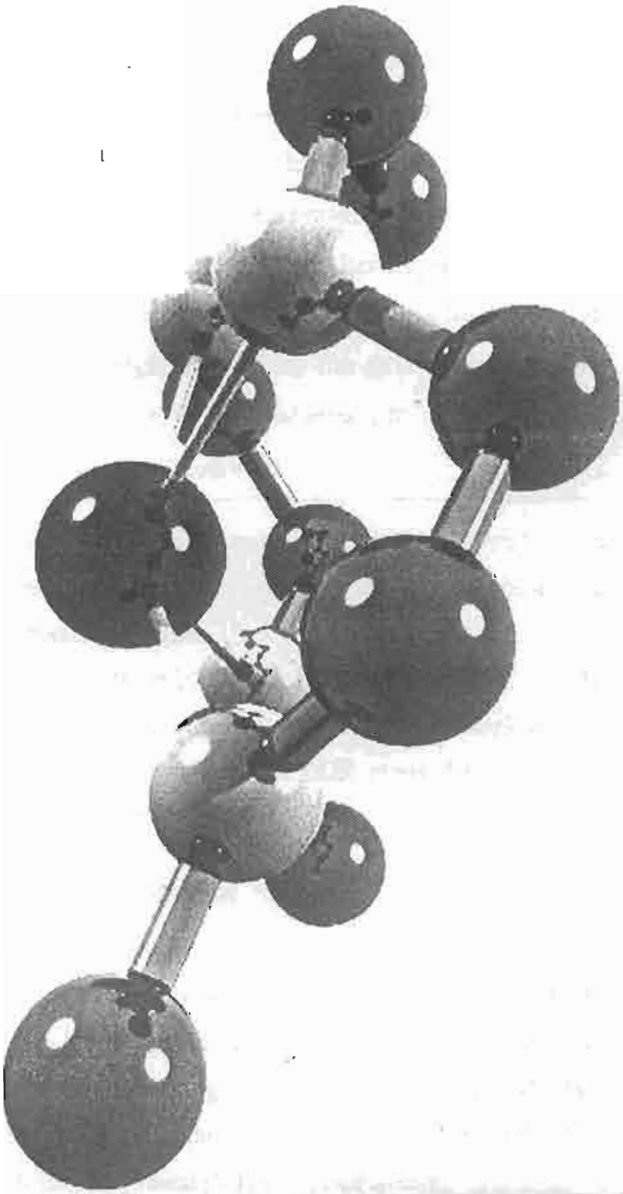

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Role of Solid-State Silane Crosslinking on Structure and Properties of Ethylene-Octene Copolymer

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Abstract

The changes in crosslink structure, rheological and mechanical properties of ethylene-octene copolymer (EOR) along the progress of silane-water crosslink reaction were investigated. The results of gel study and rheological test pointed out that the crosslink structure changes with increasing the reaction time. In the early stage, the gel content and crosslink density increased systematically with time. However, a number of polymer chains involved in the network structure hardly altered after 96 hrs of crosslinking time but more siloxane linkages occurred, leading to a systematic change in viscoelastic and tensile properties without a detection of weight change on the gel fraction. With a denser network, the crosslinked products showed an improvement in material strength.

Keywords: Silane-water crosslinking, Ethylene copolymer, Structure, Property

1. Introduction

Crosslinking is one important method for improving the high temperature properties of polymer. The silane-water crosslinking [1-3], unlike to the typical peroxide or irradiation crosslinkings, introduces the siloxane bonds between polymer chains, instead of carbon-carbon bonds (*Figure 1*).

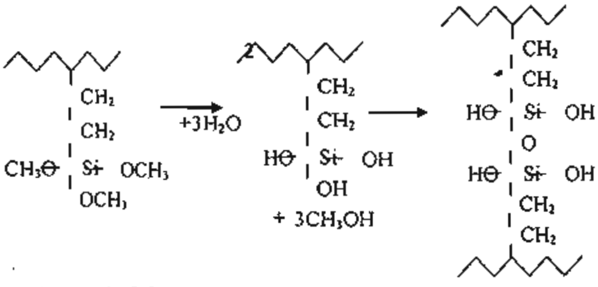

Figure 1. *Silane crosslink reaction*

Since each Si atom has three reactive groups, up to six PE macromolecules may be joined to each crosslink, which enhances the mechnical properties of the crosslinked products. The crosslink reaction also conducts while the polymer is in the solid-state. Thus the crystallinity of polymer could complicate the crosslink situation.

In this paper, we present results on the changes in crosslink structure, rheological and mechanical properties of EOR along the progress of silane-water crosslink reaction.

2. Experimental

2.1 Materials

EOR (ENGAGE E8003) with MFI of 1.0 g.10 min^{-1}, was purchased from DuPont Dow Elastomer Co. Ltd. (Wilmington, USA). The peroxide and silane used were dicumyl peroxide (DCP) and vinyl trimethoxysilane (VTMS), respectively.

2.2 Preparation of crosslinked EOR

The silane-water crosslinking process consists of two steps; i.e. silane-grafting of EOR and crosslinking of the grafted polymer. The grafting reaction of EOR with 5 %VTMS and 0.1 %DCP was carried out in a twin-screw extruder. The temperatures were carefully controlled in the range of 160-200°C, with a screw speed of 30 rpm. The grafted products were, then, immersed in hot water at 70°C to conduct a crosslink reaction. No catalyst was used in the crosslinking process.

2.3 Gel content determination

The gel content was determined according to ASTM D2765-95a. The sample was wrapped in a 120-mesh stainless steel cage and extracted in boiled xylene for 6 h. After extraction, the cage was dried in a vacuum oven. The gel content was determined from the dried content of insoluble fractions after extraction process with respect to the original sample content.

2.4 Rheological measurement

The parallel plate rheometer was operated in an oscillatory shear mode at a constant strain of 10%. The rheological behaviours were examined at 200 °C under the frequency ranged from 1 to 200 rad.s^{-1}. The complex modulus (G*) values were recorded.

For creep and recovery test, the applied stress was hold constant at a given frequency and test temperature. The resultant strain deformation was recorded. The ratio of strain values measured and constant stress was calculated, defining as the creep compliance (J).

2.5 Tensile testing

The stress-strain behaviours were determined according to ASTM D638. A crosshead speed of 500 mm.min^{-1} with a load cell of 1 kN was employed.

3. Results and discussion

The gel content determination is a widely used method for following the crosslink reaction in various systems. Figure 2 shows an increase in the gel content with increasing time. This finding is generally observed in various crosslinked systems. The rate of crosslink reaction is faster in the early stage of crosslinking. Without catalyst, the EOR reaches 80% gel after 96 hrs. of crosslinking time. Increasing the time further, the gel contents tend to level off.

Another effective way of characterising crosslink network is by determining crosslink density (ν). Based on the theory of elasticity, the number of crosslink in a unit volume or crosslink density can be predicted using the following equation: [4]

$$G^* = \nu RT$$

where R is gas constant and T is temperature.

The calculated crosslink density of EOR at 20 rad. s^{-1} is shown in Figure 3 the crosslink density does not show a plateau region as observed in the gel results, but systematically increases with increasing time.

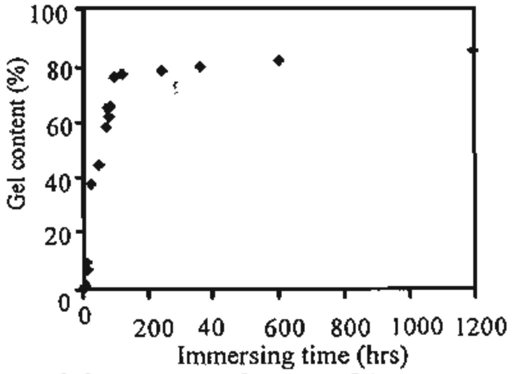

Figure 2. *Gel content as a function of time*

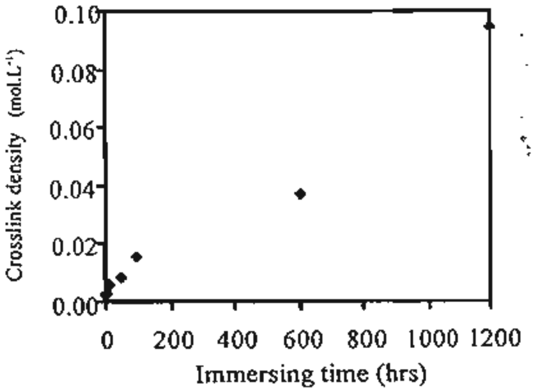

Figure 3. *Crosslink density as a function of time*

The influences of crosslink network on rheological properties can be seen from Figure 4 it is evident that all crosslinked polymers exhibit much lower magnitudes of J, compared to neat 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.

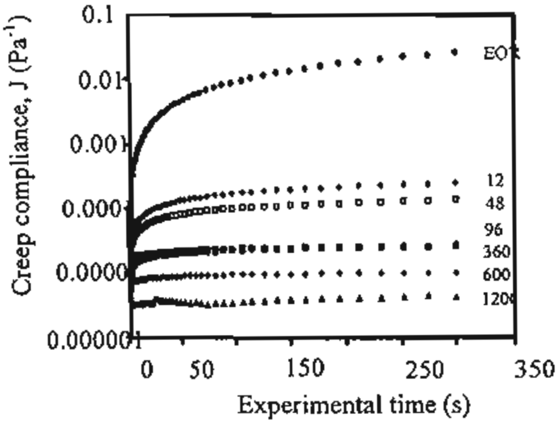

Figure 4. *Effect of crosslink on creep compliance*

The tensile results agree well with the rheological behaviours in which an increasing time of crosslinking to 360 hrs leads to a mark decrease in material extensibility without a change in gel content.

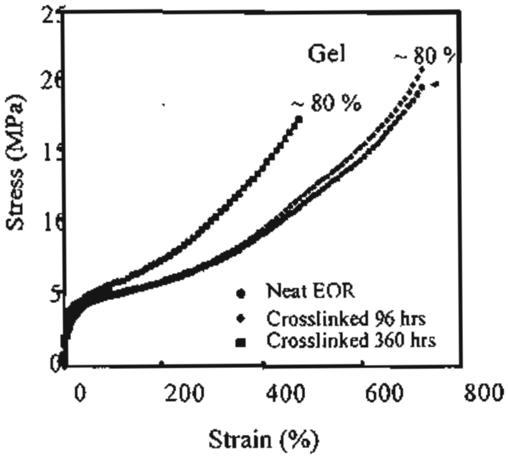

Figure 5. *Effect of crosslink on stress-strain curves*

4. Conclusion

Silane-water crosslinking of EOR was performed in the solid-state without the presence of catalyst. Increasing the time of crosslinking, the crosslink density linearly increases while the gel results show an increment in the early stage and then level off. As the network becomes denser, the changes in viscoelastic behaviours and mechanical properties are observed.

Acknowledgements

The Thailand Research Fund (TRF) and Commission on Higher Education

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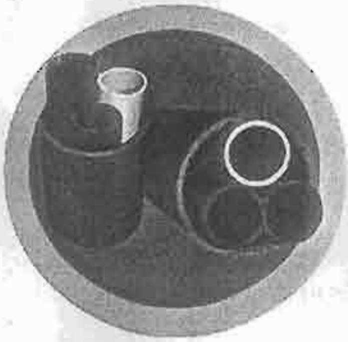

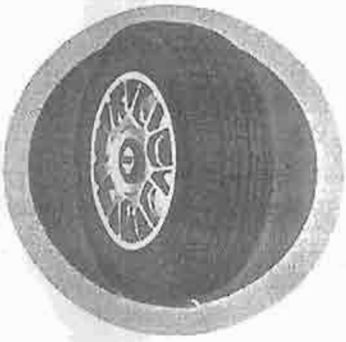

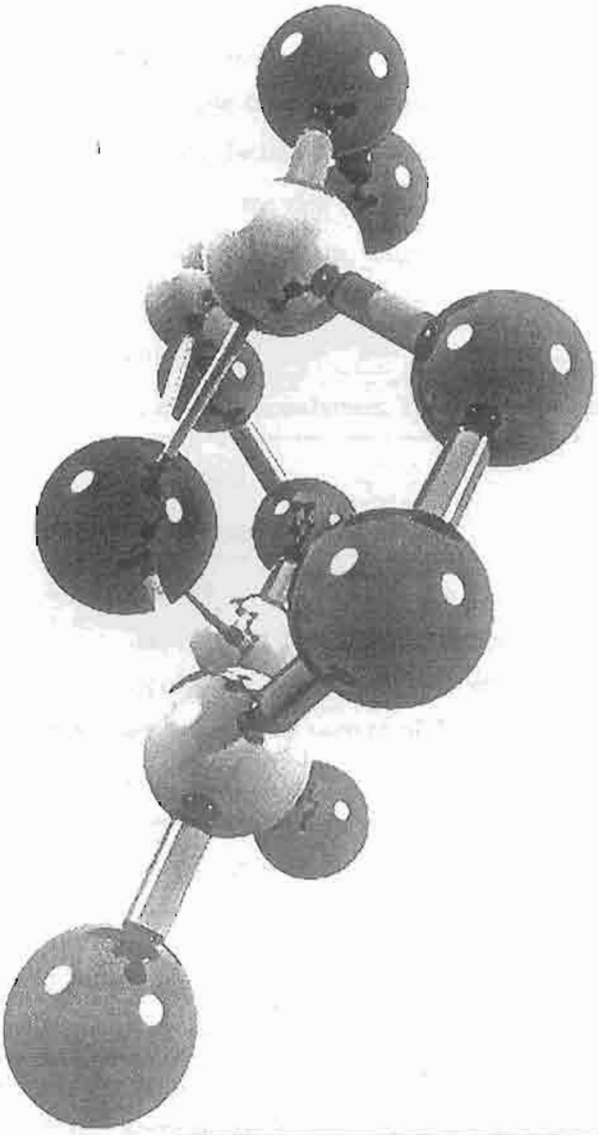

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Influence of Various Ethylene Copolymers on the Silane-Water Crosslinking of High Density Polyethylene

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Abstract

Silane-water crosslinking of high density polyethylene (HDPE) was investigated. Various ethylene copolymers including ethylene-octene copolymer, ethylene-butene copolymer and ethylene-vinyl acetate copolymer were introduced to the HDPE, in order to facilitate diffusion of water which aids crosslink reaction. The results show that the copolymers increase the rate of crosslinking of HDPE. The hydrophilicity of the copolymer plays a major role on silane crosslinking, whereas the amount of crystalline component in the copolymers shows a minor effect. After crosslinking, all crosslinked products exhibit an improvement in the thermal oxidative stability.

Keywords: Silane-water crosslinking, High density polyethylene, Ethylene copolymers, Thermal properties

1. Introduction

Properties of polymer, particularly high temperature properties, can be modified by crosslinking of the polymer chains. One method which is of interest and becomes increasingly used in the industry is a silane-water crosslinking method. Silane-water crosslinking takes place in two stages. First, a small amount of silane is grafted onto the polymer chains. The grafted polymers are subsequently shaped into finish products and then crosslinked in the presence of water. Rate and degree of crosslinking depend on several factors. One of which is the amount of crystalline component in the material. High density polyethylene (HDPE) due to its high level of crystallinity, has low silane absorption and low water diffusion. Introducing the second component having lower crystallinity is hypothesised to favor diffusion of water which aids crosslink reaction. In this study, various ethylene copolymers were analysed for their effects on structure and properties of silane-crosslinked HDPE.

2. Experimental

2.1 Materials

HDPE was from Bangkok Polyethylene Co. Ltd. Copolymers used include ethylene-octene copolymer with octene content of 7.6 %mol (EO76), and that with octene content of 10.9 %mol (EO109), ethylene-butene copolymer (EB) and ethylene-vinyl acetate copolymer with vinyl acetate content of 18 %wt (EVA).

2.2 Preparation of crosslinked polymers

HDPE and its blends with various copolymers in the ratio of 80/20 were prepared in a Haake Rheocord batch mixer. The grafting reactions of the blends were carried out at 170°C using 5 % vinyl trimethoxysilane and 0.1 % dicumyl peroxide. The grafted products were then compression-molded into 1 mm thick sheets. The sheets were subsequently immersed in hot water at 70°C for conducting a crosslink reaction. No catalyst was used in accelerating reaction.

2.3 FTIR analysis

Fourier Transform Infrared (FTIR) spectra were recorded from a Perkin-Elmer spectrophotometer in the wavenumber range from 4000-600 cm^{-1}.

2.4 Solvent extraction

The amount of crosslink was reported in a term of gel content which was determined from the insoluble fraction of silane-crosslinked polymers after extraction in refluxing xylene according to ASTM D2765-95a. The crosslinking rate was calculated from the slope of the graph plotted between gel content and immersing time in the initial crosslinking time between 0-12 hrs.

2.5 Differential scanning calorimetry

The thermal behaviors of samples were studied by a Perkin-Elmer DSC-7. The samples were heated from 50 to 170°C at a scan rate of 20°C.min^{-1}. The crystallinity (χ_c) was calculated by taking the values of heat of fusion (ΔH_f) divided by the enthalpy required for 100 % crystallinity which is equal to 290 J.g^{-1}. [1]

2.6 Thermogravimetric analysis

The thermogravimetric experiments were performed using a Perkin-Elmer TGA-7 thermal analyzer. The samples were heated from 40 to 600 °C using a heating rate of 20 °C.min^{-1}, with a controlled oxygen flow of 60 ml.min^{-1}.

3. Results and discussion

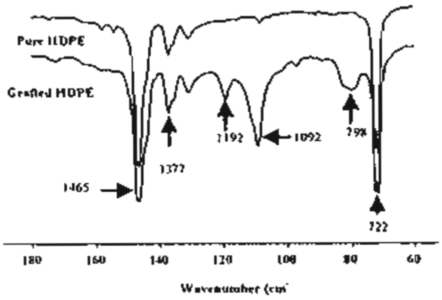

Figure 1. *FTIR spectra of unmodified and silane grafted HDPE*

Figure 1 shows the FTIR spectra of HDPE before and after silane-grafting reaction. The peaks at 798, 1092 and 1192 cm^{-1} corresponded to the absorption of methoxysilane group ($Si\text{-}OCH_3$) clearly reveal the presence of silane units in the samples.

Table 1. *The grafting index of various blends*

Sample	Grafting index
Si-g-HDPE	1.94 ± 0.04
Si-g-HDPE/EO76	1.58 ± 0.05
Si-g-HDPE/EO109	1.14 ± 0.02
Si-g-HDPE/EB	1.74 ± 0.06
Si-g-HDPE/EVA	0.73 ± 0.04

The degree of grafting in a term of grafting index was then calculated from the relative intensity of absorption peak at 1092 cm^{-1} to that of the reference peak at 1377 cm^{-1}. The results of Table 1 show a reduction in a degree of grafting caused by the presence of copolymers.

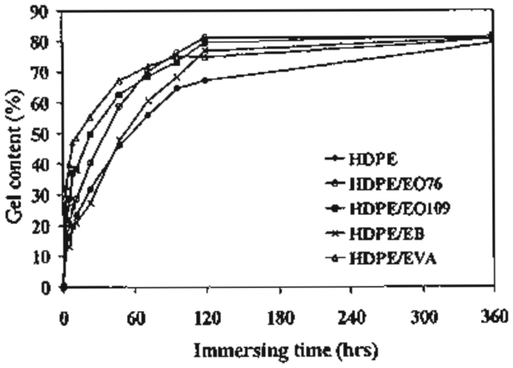

Figure 2. *Gel content of various crosslinked samples*

By immersing the silane-grafted polymers in water, the methoxy groups (Si-OCH$_3$) were hydrolysed and formed into the silanol groups (Si-OH). These silanol groups were then condensed and the siloxane (Si-O-Si) crosslink network was obtained. As shown in Figure 2, the amount of gel increases with increasing time. The same trend is observed in all blends but with difference in magnitude of gel content. The incorporation of ethylene copolymers clearly increases the rate of crosslinking.

Table 2. *Gel content and crosslinking rate of various crosslinked samples*

Samples	Gel content^a (%)	Crosslinking rate (%. hr^{-1})
HDPE	79.10	1.77
HDPE/EO76	80.87	2.23
HDPE/EO109	81.66	3.04
HDPE/EB	80.83	1.65
HDPE/EVA	80.33	3.69

^{a} : determined after 360 hrs of crosslinking time

Table 3. *Effect of crosslink on percentage of crystallinity*

Samples	Decomposition temperature (°C)	
	Before crosslinking	After crosslinking for 360 hrs
HDPE	413	448
HDPE/EO76	412	441
HDPE/EO109	416	440
HDPE/EB	414	439
HDPE/EVA	417	445

The highest rate is found in the case of HDPE/EVA blends, followed by HDPE/EO109, HDPE/EO76, and HDPE/EB, respectively (Table 2). These results point out that the structure and properties of ethylene copolymers play significant role in crosslinking of HDPE. EVA with its polar groups in the molecules has a strong ability for water diffusion. EO, although, is a hydrophobic material, increases diffusion of water in HDPE due to its low crystalline content (Table 3).

Table 4. *Effect of crosslink on decomposition temperature*

Samples	% Crystallinity	
	Before crosslinking	After crosslinking for 360 hrs
HDPE	61	61
HDPE/EO76	49	47
HDPE/EO109	49	50
HDPE/EB	50	50
HDPE/EVA	49	50

Table 4 demonstrates the results on the decomposition temperature of silane-crosslinked HDPE. It could be seen that the decomposition temperatures can be significantly increased by introducing a crosslink network into the system. A slight decrease in thermal oxidative stability of HDPE was resulted when incorporating the copolymers in the systems.

4. Conclusion

The silane-water crosslinked HDPE was prepared. The effects of various ethylene copolymers on the structure and properties of crosslinked HDPE were studied using FTIR measurements, solvent extraction, DSC and TGA techniques. The incorporation of copolymers was found to increase the crosslinking rate of HDPE. The highest rate was found in HDPE/EVA blends, followed by HDPE/EO109, HDPE/EO76, and HDPE/EB, respectively. The results pointed out that the hydrophilicity plays a major role whereas the amount of crystalline portion has a minor effect on the silane crosslinking. The thermal oxidative stability of HDPE was found to be improved by crosslinking. A slight decrease in this property was observed after introduction of the copolymers.

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