Thermal Property Improvement of Ethylene-Octene Copolymer through the Combined Introduction of Filler and Silane Crosslink

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ABSTRACT: In many applications, e.g., wire and cable insulation, hot water pipe, high-temperature properties of polymer are essential. This article presents the use of silane crosslinking together with the addition of particular filler in improving the thermal and mechanical properties of ethylene-octene copolymer (EOC). The effects of filler surface characteristics on siloxane network structure developed and final properties of the crosslinked products are discussed. The results show an increase in the decomposition temperature of EOC more than 50°C after modification. Only crosslinked composites are able to withstand the high-temperature environment of aging test which is beyond the melting temperature of the matrix polymer. The crosslinked composites filled with calcium carbonate show superior properties to those with silica, due to a higher crosslink density and tighter network structure formed. The silane coupling mechanism and the presence of bound polymer on silica surfaces cause difficulties for the crosslink formation in the silica filled systems. However, an advantageous influence of both silane coupling and crosslink reaction in the silica filled composites is seen on the enhanced tensile strength and modulus of the materials. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 424–430, 2010

Key words: crosslinking; composites; thermal properties; mechanical properties

INTRODUCTION

Polymer properties could be modified by a number of ways. Introduction of particulate fillers to polymers usually results in an improvement of composite modulus and strength. The properties of filled composites depend markedly on the interaction between polymer and filler. One possible role to improve the interaction is to modify the filler surfaces to be more compatible with polymer matrix.[1-4] The use of stearic acid coating on the surface of calcium carbonate ($CaCO_3$) reveals a drastic decrease in filler surface energy[5] and results in better processability and well-filler dispersion.[2,6] Silane-coupling agent is also in widespread use for modifying the surface of mineral filler with high concentrations of reactive hydroxyls such as silica.[7,8]

Crosslinking is another effective way of improving the polymer properties, especially the high-temperature properties[9] and properties during long-term loading.[10] The use of silane technology in crosslinking polyolefin and its copolymers as well as its composites has been reported.[11-22] The silane-crosslinked materials are used worldwide in producing cables, hot-water pipes, foams, etc. The silane–water crosslinking process involves free radical grafting of vinyl alkoxysilane onto polymer backbone and subsequent self-condensation of hydrolysable alkoxysilane groups in the presence of water to form crosslink network through siloxane linkages as shown in Figure 1. The effective alkoxy silanes are vinyl trimethoxysilane (VTMS) and vinyl triethoxysilane (VTES). However, the former is more preferred due to its higher reactivity with water during crosslink reaction.[23] In this study, VTMS was used. In our previous study, it has been shown that the degree of water crosslinking is significantly affected by degree of silane grafting and crosslinking time, whereas the crosslinking rate depends strongly on the amount of crystalline and amorphous portions in the polymers.[12-14] The crosslink structure and content play a major role in determining the high- temperature properties of polymer.[11,16-18] Benefits of silane–water crosslink on mechanical properties of polymers have also been reported.[11,16,19-21] Shah et al.[16] studied the effects of silane content on the mechanical properties of silane–water crosslinked PE and found that the tensile strength of crosslinked product increases with increasing silane content up to 5 phr. Our previous study showed the enhancement of composite modulus, tensile strength, heat distortion, and
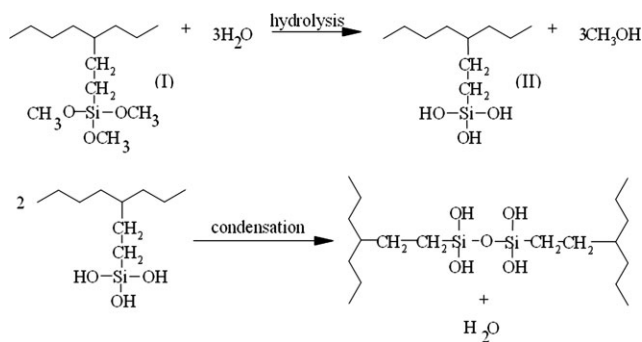
Figure 1 Silane–water crosslink reaction.

decomposition temperatures when introducing siloxane network into the polypropylene composites filled with CaCO$_3$.[19] These improvements have been found also in the system of silane-crosslinked PE composites filled with nanotube.[20] Although, in the wood–polymer composites, the silane–water crosslink was reported to improve the interfacial strength between wood fiber and polymeric matrix, resulting in an improvement of flexural strength and its thermal durability.[21]

The present work aims to investigate the combined effects of silane crosslinking and filler addition on the development of silane crosslink structure and resultant properties of ethylene-octene copolymer (EOC) composites. Two fillers differing in their surface property were studied, namely stearic-acid-coated CaCO$_3$ as a nonreactive particulate and precipitate silica as a reactive filler which has functional groups that could be reacted with alkoxysilane reagent during the silane grafting and crosslinking process. Changes in tensile properties, thermal aging, and thermal decomposition behaviors of the composites brought about by filler addition and crosslink network developed are discussed.

EXPERIMENTAL

Materials

Metallocene EOC (Engage E8003) with a MFI of 1.0 g 10 min^{-1} was purchased from DuPont Dow Elastomer (Wilmington, DE). CaCO$_3$ (Turboplex 7227) with 2 % wt stearic acid surface coating was supplied by Lime Quality (Bangkok, Thailand). Its specific density and specific surface area were 2.7 g cm^{-3} and 22 m^2 g^{-1}, respectively. Silica (Tokusil 233) with bulk density of 0.240 ± 0.025 g cm^{-3} and specific surface area of approximately 145 m^2 g^{-1} was from Tokoyama Siam Silica. (Bangkok, Thailand). Dicumyl peroxide (DCP) as an initiator and VTMS as a monomer for the grafting reaction were purchased from Aldrich Chemical (Milwaukee, Switzerland) and used without purification.

Preparation of crosslinked composites

The polymer/filler composites in the weight ratio of 80/20 were prepared in a TSE16 twin-screw extruder (Prism, Staffordshire, UK). The fillers were dried for 24 h in a hot-air oven prior to compounding. The temperatures were set in a range of 160–200 °C. The compounds obtained were then tumble mixed with 5.0 % wt VTMS and 0.1 % wt DCP in a sealed container and kept overnight under N$_2$ atmosphere. The prepared compounds were then taken into the extruder for conducting a grafting reaction. A screw speed of 30 rpm with a temperature profile of 160, 200, 170, 170, and 170°C from feed zone to die zone were carefully controlled. The grafted composites obtained were then shaped by compression molding at 190°C into 1-mm thick sheets. To conduct a water-crosslink reaction, the molded samples were immersed in hot water at 70°C for a specified time.

Characterization and testing

Fourier Transform Infrared (FTIR) spectroscopy was used to analyze the presence of silane in the grafted products. Films of 50-µm thick were washed with an excess volume of acetone to remove unreacted silane and residual peroxide prior to FTIR measurement. The IR spectra were recorded using a Perkin Elmer system 2000 FTIR spectrometer (Boston, MA) in the range of 600–4000 cm^{-1} with a resolution of 4 cm^{-1}.

The gel content or insoluble fraction in either crosslinked materials or grafted products as a result from self-crosslinking of the polymer macroradicals was determined using solvent extraction method 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 until constant weight. The gel content was calculated using the following equation.

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

The parallel plate rheometer (Anton Paar MCR500, Stuttgart, Germany) was operated in an oscillatory shear mode at a constant strain within the linear viscoelastic region of 10%. The samples used in the test were fabricated in a disc with 1 mm in thickness. The rheological behaviors were examined at 200°C under the frequency ranged from 1 to 200 rad s^{-1}. The values of complex modulus (G^*) were recorded and then used in the calculation of the crosslink density (v) based on the theory of elasticity where the

number of crosslink in a unit volume can be predicted using the following equation.

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

where R is gas law constant ($8.3144 \text{ J mol}^{-1}\text{K}^{-1}$) and T is temperature (473 K). This equation has been successfully applied to determine the crosslink content in the system of E-beam crosslinked LDPE[22] and to explain the crosslink phenomenon in silane-crosslinked materials as well.[24]

The tensile test was carried out using an Instron universal tensile tester Model 5569, with a crosshead speed of 500 mm min^{-1} and a 1 kN load cell according to ASTM D638-03. The dumbbell specimens of 1-mm thick were stamped cut from a compression-molded sheet. The tensile strength, elongation at break, and modulus at 300% strain were reported. To study the thermal aging properties of crosslinked materials, the specimens were hanged in a hot-air oven at 110°C for 12 h before measuring their tensile properties using the same testing conditions as those used for the unaged specimens. All reported results were an average from at least five specimens.

Thermal decomposition investigation was performed through a thermal gravimetric analyzer (Mettler Toledo SDTA851, Schwerzenbach, Switzerland). The apparatus was continually purged with oxygen gas. A sample (6 + 1 mg) was placed in a platinum sample pan, and then heated from 40 to 650°C at the rate of 10°C min^{-1}. The weight percentages of samples were measured as a function of temperature. The decomposition temperature at 10% weight loss (T_d) was reported.

RESULTS AND DISCUSSION

Compounding and grafting process

Table I shows the processing torque and pressure during composite preparation and grafting process, together with the amount of insoluble portion in the prepared composites after xylene extraction. Compared to the neat EOC, the processing torque and pressure increase slightly with the addition of fillers. The magnitude of torque increment is higher in the case of silica-filled composite. This result is attributed to a larger specific surface area of silica structure and its aggregate structure due to silanol group on its surfaces which renders a formation of adsorbed polymer on its porous surface. The structure of the formed polymer inside the composites filled with silica particles has been proposed earlier[25] where unbound and bound polymers are present. The bound polymer is the portion of polymer chains which are trapped on the filler surfaces and is hardly dissolved by polymer solvent. To verify

TABLE I
Processing Torque and Pressure, Insoluble Portion after Xylene Extraction, and Mechanical Properties of Various Filled Composites and Their Grafted Samples

System	Torque (N m)		Pressure (Psi)		Insoluble portion (%)		Tensile strength at break (MPa)		Elongation at break (%)		Modulus (MPa)	
	Before grafting	After grafting	Before grafting	After grafting	Before grafting	After grafting	Before grafting	After grafting	Before grafting	After grafting	Before grafting	After grafting
EOC	10–11	11–12	4–5	4–5	0.11 (0.02)[a]	0.18 (0.04)	23.80 (1.39)	19.89 (1.17)	738 (13)	742 (24)	7.83 (0.43)	7.00 (0.27)
EOC/CaCO$_3$	14–16	15–16	7–8	7–8	0.41 (0.15)	0.37 (0.12)	24.81 (0.71)	24.17 (0.92)	770 (13)	763 (15)	7.41 (0.15)	7.72 (0.07)
EOC/silica	20–21	20–21	8–9	9–10	2.05 (0.15)	2.38 (0.11)	11.75 (0.76)	17.23 (0.50)	420 (14)	331 (10)	8.77 (0.34)	16.24 (0.60)

[a] Standard deviation in parentheses.

that bound polymer exists in the silica-filled system, the composite was extracted with hot xylene and the content of insoluble portion was then determined. As demonstrated in Table I, silica-filled EOC composite (EOC/silica) exhibits the insoluble portion of about 2 % wt before grafting reaction, indicating the presence of bound polymer on the silica particles.

In this study, a silane-grafting reaction of filled composites was conducted when the polymers are in molten state inside a twin-screw extruder. During a grafting reaction, a recombination of polymer macroradicals may occur as a side reaction.[13,15] This might result in a crosslink in the system and lead to a processing difficulty. From Table I, processing torque and pressure during the preparation of the grafted composites are found to be similar to those of the ungrafted composites. This points out that the silane-grafting process is efficiently controlled and a side reaction from the peroxide-induced crosslinking of EOC is negligible. The data of insoluble content confirm this point.

FTIR analysis of grafted composites

Figure 2 shows the FTIR spectra of EOC samples before and after modification. The feature peaks appeared at 1377 cm^{-1} and 1465 cm^{-1} correspond to the C—H bending vibrations of the methyl and methylene groups of EOC, respectively. The incorporation of CaCO$_3$ into EOC leads to the appearance of sharp absorption peak at 1797 cm^{-1} that is the energy absorption occurred in CO$_3^-$ ion (bending mode).[2] For the silica-filled composites, the broaden absorption peak ranged from 1000 cm^{-1} to 1200 cm^{-1} is clearly seen and assigned to the characteristic of SiO$_4$.[23] After introducing the silane unit, the peaks of trimethoxysilane groups (Si—(O—CH$_3$)$_3$) appear at 803 cm^{-1} and 1092 cm^{-1} for the grafted EOC composites filled with CaCO$_3$, whereas, in the

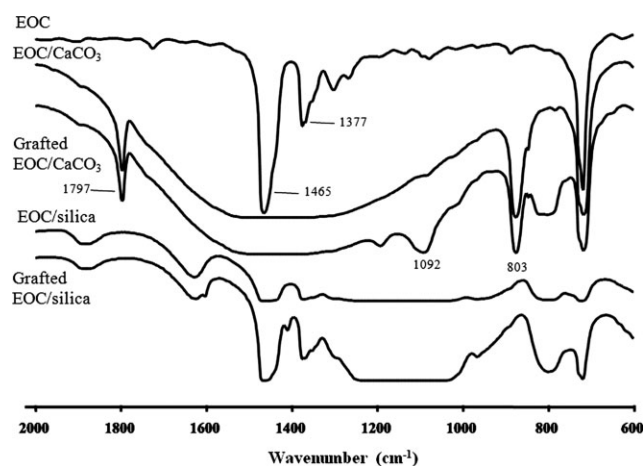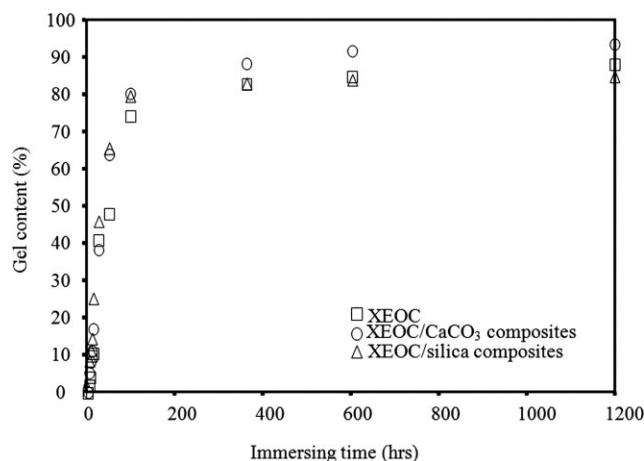**Figure 3** Effect of CaCO$_3$ and silica filler on gel content.

silica filled system, it is difficult to identify the position of Si—OCH$_3$ peaks due to the resemblance between Si—OCH$_3$ structure and silica structure, which is composed of SiO$_4$.

Water-crosslinking process

Figure 3 illustrates the effect of CaCO$_3$ and silica fillers on the gel content as a function of crosslinking time. As can be seen, the tendency of gel content in both crosslinked composites is very similar to unfilled system in which the gel content increases sharply with increasing crosslinking time up to about 100 h and levels off thereafter. When compared among crosslinked systems, the magnitude of gel content in the composites filled with CaCO$_3$ ($\sim$ 90% gel) seems to be slightly higher with respect to others (80–85% gel).

Figure 4 shows the calculated crosslink density of various crosslinked samples as a function of
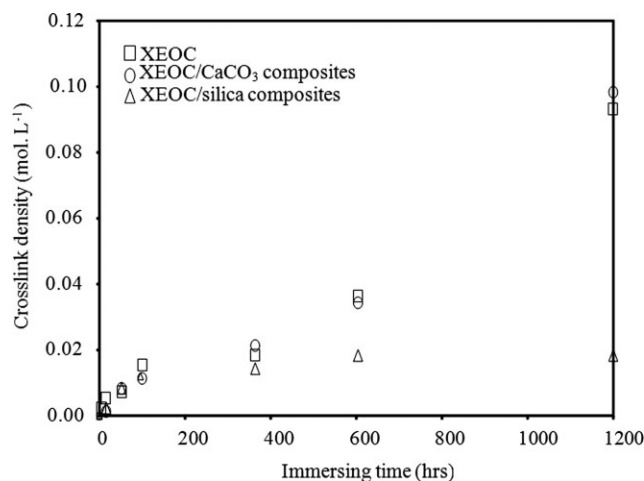
Figure 2 FTIR spectra of EOC before and after modification.

Figure 4 Crosslink density as a function of crosslinking time.

crosslinking time. The results reveal a linear increase in crosslink density with increasing time for the unfilled and CaCO$_3$-filled composites. This is as expected since as the crosslink reaction was conducted, a number of polymer chains form into a crosslink network. Increasing time of the process leads to more polymer chains involved in the reaction. As a result, the contents of gel and crosslink density increase systematically. The composites are now characterized by a structure of loosely crosslink network. Increasing the reaction time further, crosslink density carries on increasing but the gel content seems to be leveled off. At this stage, more crosslink points are believed to take place within an existing gel. The network then becomes denser (tight network). In the case of silica-filled system, a systematic increase in crosslink density is only observed in the early stage of crosslinking time approximately up to 100 h. The crosslink density and gel content hardly change after increasing the time of crosslink process beyond that period. Compared to the unfilled and CaCO$_3$-filled systems, the silica-filled composite exhibits a much lower crosslink density. It is believed here that there is a possibility of silane coupling occurred in the silica-filled system[7,8] which renders a less available silane unit for silane-crosslink reaction. Also, in this study, bound polymer is found to be formed on the silica surfaces and this might restrict the freedom of polymer chain movement to be involved in the crosslink reaction. The amount of insoluble portion (bound polymers) in various systems is shown in Table I. As a result, silane crosslinking in the silica-filled composites is more difficult than that in the carbonate-filled systems and only a loosely crosslink network could be formed in the final stage of crosslink process.

Tensile properties

The tensile properties of unfilled EOC and its composites filled with CaCO$_3$ and silica are shown in Table I and Figure 5. Neat EOC used in this study exhibits an elastomeric nature under tensile loading where a gradual increase in stress thereafter applying force and high magnitude of elongation are observed. Such characteristics remain even after the filler addition, but difference in magnitude of stress and elongation is found. The unfilled EOC and its composite with CaCO$_3$ filler reveal much higher magnitude of stress and elongation, with respect to the composite filled with silica. This is partly due to a trapping of some polymer segment in the silica structure causing a restriction of polymer chain movement. When the stress is applied, these chains are unable to dissipate energy, thus, leading to a high local stress in the sample. As a consequence,
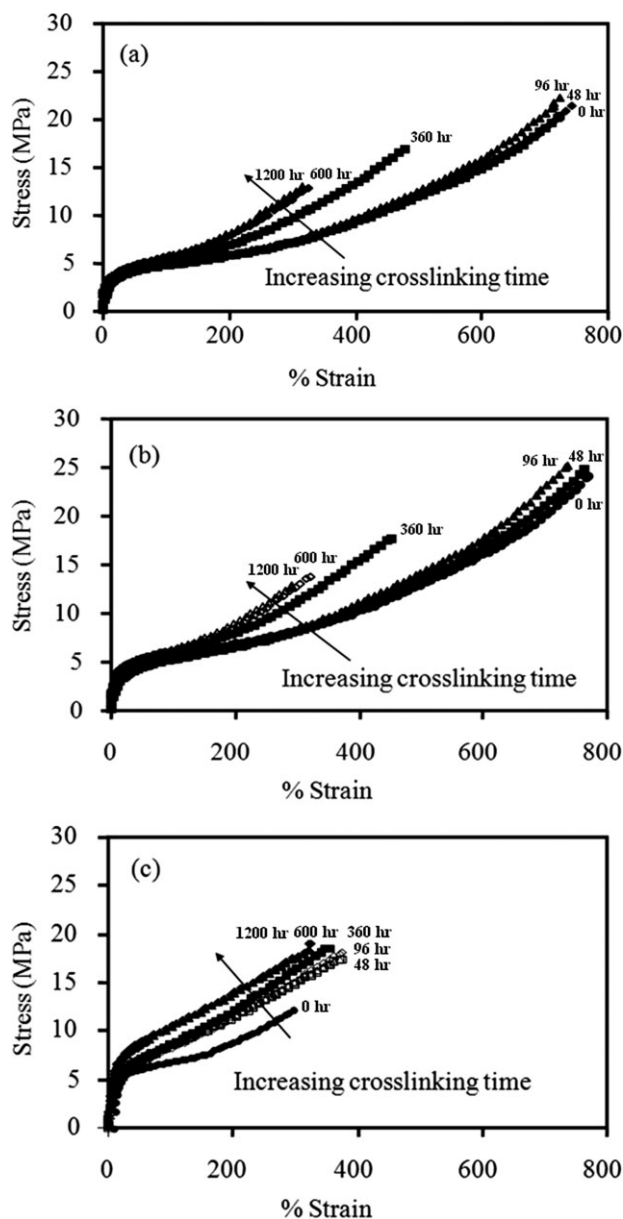

Figure 5 Stress–strain curves of (a) crosslinked EOC, (b) crosslinked EOC/CaCO$_3$, and (c) crosslinked EOC/silica composites.

the deterioration in elongation at break is observed in the silica-filled system.

The introducing of the silane units to EOC causes only slight effect on the tensile properties. A similar trend is found also for the CaCO$_3$-filled system where the tensile strength, elongation at break, and modulus of the grafted composites hardly change after the grafting reaction. This is unlike to the results found for the silica-filled system. The improvement of tensile strength and modulus is resulted together with a slight deterioration in elongation at break. The coupling reaction between silanol groups on the silica surface and those of silane units on the polymer chains is believed to be responsible for this finding,

resulting in an improved filler-polymer interaction and a higher constraint in molecular mobility of the system. A similar finding was reported in the silane-grafting wood–polymer composites.[21]

Figure 5 shows the stress–strain curves of various crosslinked systems. Changes in tensile behaviors are clearly seen after conducting a crosslink reaction for different durations, especially in the systems of unfilled EOC and $CaCO_3$-filled composites. The crosslinking time shows strong influence on these properties. As the crosslinking time increases, the magnitude of property changes become increasing. It is believed here that for the water-crosslinking process where the reaction is performed when the polymer is in a solid state, the mobility of polymer chains may be restricted and thus longer time is required to obtain a product with highly crosslink. Therefore, the samples that are crosslinked for a shorter period (crosslinking time $\leq$ 100 h) are still able to deform and behave similarly to the neat samples. Those samples contain only loose crosslink network. On the other hand, the samples with tight network (crosslinking time > 100 h) need more stress to deform and eventually the failure occurs with the increments of modulus and the reduction of elongation and tensile strength at break. A similar finding on the effect of crosslink structure on the tensile properties of LDPE and EOC systems has been reported.[12,24] In the case of silica-filled system, both tensile strength and modulus improve considerably thereafter conducting a crosslinking process. This reveals an advantageous influence of both silane coupling and crosslink reactions through siloxane linkages on the enhancement of mechanical properties of the composites.

Thermal aging and thermal decomposition behavior

The filled composites that are crosslinked are advantageous when they are placed in high-temperature environments where the composites may be exposed to temperatures exceeding the melting temperature of the composite polymer. In this study, the thermal agingbehaviors of all silane-crosslinked samples were investigated by monitoring the changes in their tensile behaviors before and after aging test at 110°C. It is found that the uncrosslinked sample fails to withstand the heat. The sample was deformed and became soft thereafter heating in a hot-air oven for a short period of time (5 min). This is as expected since the aging temperature used in this study (110°C) was much higher than the T_m of EOC (87°C). The presence of either $CaCO_3$ or silica particles in the polymer matrix does not beneficially affected on the thermal aging properties of the matrix polymer. Only the crosslinked sample can
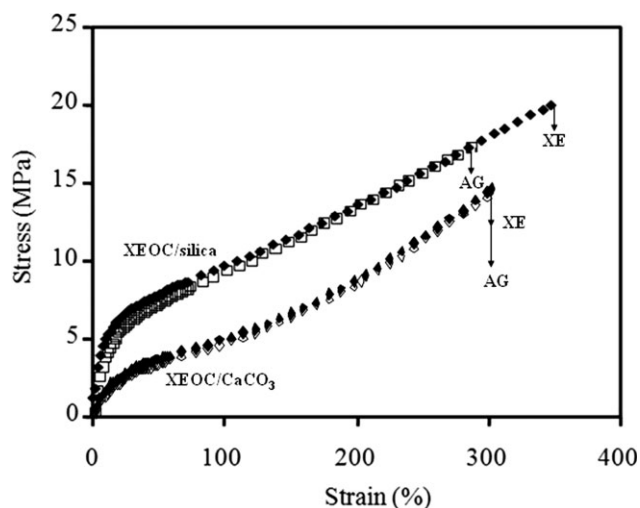

Figure 6 Stress–strain curves of crosslinked EOC filled with $CaCO_3$ and silica before (XE) and after thermal aging (AG). The samples were crosslinked at 70°C for 1200 h.

withstand such a high-temperature environment. Therefore, the aging properties only of the crosslinked samples are reported here.

Figure 6 demonstrates the tensile properties of materials crosslinked for 1200 h after aging test (AG) compared to unaged sample (XE). No reduction in tensile modulus, strength, and elongation is observed after aging test at 110°C in the case of crosslinked composites filled with $CaCO_3$. In such composites, a tight network is believed to be formed in which gel content of approximately 90% and crosslink density of 0.099 mol L^{-1} are found. Although in the silica-filled system crosslinked for the same duration, a crosslink density of only 0.019 mol L^{-1} is observed. As a consequence of lower crosslink density and loose network structure, poorer tensile aging properties are resulted for the silica-filled composites. However, such crosslinked silica composites still exhibit a much better thermal aging properties with respect to the uncrosslinked samples. The degree of crosslink and structure of network (loose or tight) developed inside the composites certainly play a crucial role to tailor the high-temperature properties of polymer.

Figure 7 illustrates the TGA thermograms of EOC composites filled with either $CaCO_3$ or silica and their crosslinked products. Neat EOC exhibits one decomposition step with a T_d of 360°C. Both filled composites reveal two decomposition steps where the residual weight loss is verifiable for the amount of filler in the composites. A shift of majority decomposition stage to higher temperature is evident in both the composites system. The addition of $CaCO_3$ and silica fillers to EOC leads to the composites with T_d of 386 and 360°C, respectively. An increment is more apparently in the case of crosslinked materials.
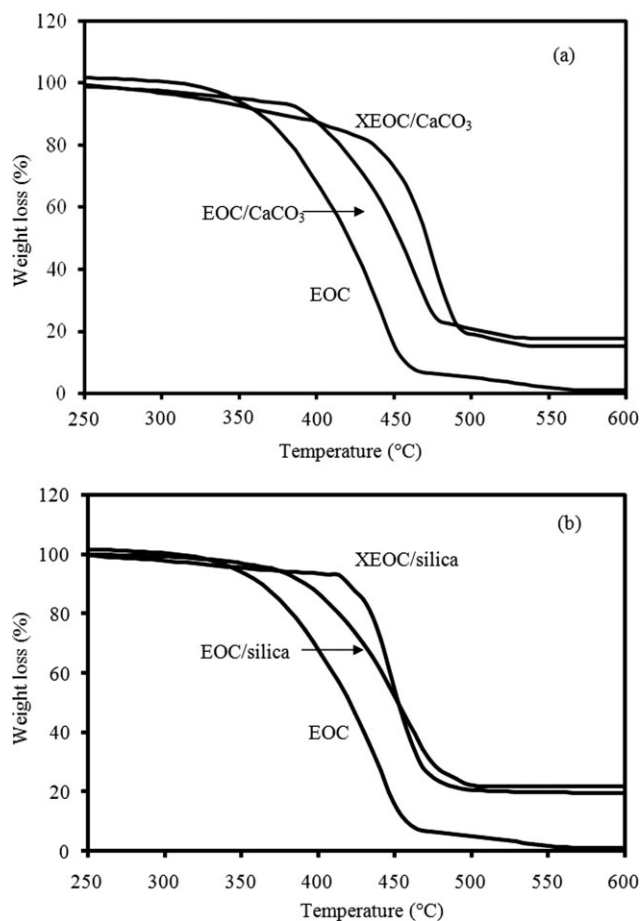
Figure 7 TGA traces of EOC composites filled with (a) CaCO₃, (b) silica, and their crosslinked products.

A considerable advantage of combined use of filler into polymer matrix together with the presence of siloxane network is clearly revealed in the improvement of thermal decomposition behavior of polymer. A much higher decomposition temperature of 415°C is observed in the case of crosslinked composites filled with CaCO₃. This is believed to be mainly due to a higher crosslink density in the CaCO₃-filled system. For the silica-filled system, crosslinked sample reveals uniform decomposition behavior with a T_d of 390°C.

CONCLUSIONS

Improvement in mechanical and thermal properties of EOC was achieved by combined introduction of filler and siloxane-crosslink network in the systems. The filler characteristic and crosslinking time were proved to be crucial factors in tailoring the structure of network developed in the composites and the properties of resultant materials. The crosslinked

composites filled with CaCO₃ showed much higher crosslink density than that containing silica filler. A tight network is believed to be formed in such composites. A coupling reaction between silanol groups on silica surface and those of silane units on the polymer chains caused less available silane units for crosslink reaction. The presence of bound polymer on the silica surfaces also limited the crosslink formation. However, an advantageous influence of both silane coupling and crosslink reaction in the silica-filled composite was clearly seen on the enhanced tensile strength and modulus of the materials. Apart from the mechanical property improvement, an increment of T_d more than 50°C was found for the crosslinked composites filled with CaCO₃. Such crosslinked composites are also able to withstand the high-temperature environment of aging test which is beyond the melting temperature of the matrix polymer.

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