

Performance Evaluation of Silane Crosslinking of Metallocene-Based Polyethylene–Octene Elastomer

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ABSTRACT: Vinyl trimethoxysilane (VTMS) was grafted onto metallocene-based polyethylene–octene elastomer (POE) using a free-radical reaction of VTMS and dicumyl peroxide as an initiator, and then the grafted POE was crosslinked in the presence of water. The effects of VTMS concentration on crystallization behavior, mechanical properties, and thermal properties of POE before and after crosslinking were studied in this article. Multiple melting behaviors were found for POE after silane crosslinking by using DSC measurement. Degree of crystallization of silane-crosslinked POE decreases from 18.0 to 14.3%, with increase of VTMS from 0

to 2.0 phr. Tensile strength of silane-crosslinked POE reaches a maximum of 28.4 MPa when concentration of VTMS is 1.5 phr, while elongation at break is 487%. TG shows that the temperature of 10% weight loss for pure POE is 405°C, while for crosslinked POE with addition of 2.0 phr VTMS the value comes to 452°C, indicating that crosslinking significantly help improve the thermal stability of POE. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5057–5061, 2006

Key words: polyethylene–octene elastomer; silane; crosslinking; melt; crystallization

INTRODUCTION

Metallocene-based polyethylene–octene elastomer (POE), developed by using a metallocene catalyst by Dow and Exxon, has received much attention in recent years, due to its unique uniform distribution of comonomer content and narrow molecular weight distribution.^{1,2} POE has fast mixing and better dispersion properties when compared with the conventional elastomers, such as ethylene–propylene copolymer and ethylene–propylene–diene copolymer.³ Whereas, there are some natural shortcomings of pure POE, which are the limits of thermal stability and large permanent distortion. Crosslinking technology provides an important method to improve the thermal and chemical resistance of polyolefins. In addition to the usual peroxide crosslinking or irradiation crosslinking, the utilization of silane–water crosslinking has gained much attention in recent years because of its various advantages, such as easy processing, low capital investment, and favorable properties in the processed materials. In producing silane crosslinkable polyolefins, a peroxide, a silane (e.g., vinyl trialkoxy silane), and polyolefins are mixed by a melt process. During the process, the silane is grafted onto the backbones of polyolefins via free radicals, then the silane-

grafted polymers are hydrolyzed and crosslinked by forming Si–O–Si linkages. In recent years, silane crosslinking polyolefins have been widely used to produce wire and cable insulation, water heating pipes, and weather stripping, etc.^{4–7}

As so far, some literatures about the grafting and crosslinking of POE have been published. Wu et al.⁸ studied the grafting of maleic anhydride onto POE, and Liao and Wu⁹ studied the peroxide crosslinking of POE. As for the silane crosslinking of POE, very few papers can be found in the literature. Sirisinha and Meksawat^{5–7} studied the differences between peroxide-crosslinked POE and vinyl trimethoxysilane (VTMS)-crosslinked POE, in terms of processing and product mechanical and thermal properties, and also investigated the change in properties of silane–water-crosslinked POE after prolonged crosslinking time. Jiao et al.¹⁰ reported the silane crosslinking of ethylene–octene copolymer, focusing on different silanes.

In the present article, silane crosslinking technology was used to modify POE to achieve optimal properties of POE such as better thermal stability, better mechanical performance, and so on. First, silane-grafted POE was prepared using a free radical reaction of VTMS and dicumyl peroxide (DCP) as an initiator, crosslinking reaction was then conducted in presence of water. The crosslinking reaction involves hydrolysis of the alkoxy groups by moisture, followed by condensation of the hydroxyl groups formed to form stable siloxane linkages, thus silane-crosslinked POE was obtained. Mechanical properties, thermal properties,

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and crystallization behavior of POE before and after crosslinking were studied.

EXPERIMENTAL

Materials

POE (Exact 0203) used here was supplied by Exxon-Mobil Corp. (USA), and its properties are presented in Table I.¹¹ Vinyl trimethoxysilane (VTMS, Z-6300) was supplied by Dow Corning Corp. (Midland, MI, USA). Dicumyl peroxide (DCP) used here was a type of analytical pure, provided by Shanghai Gaoqiao Chemical Corp. (China). Catalyst used here was dibutyltin dilaurate (DBTL), purchased from Atofina Corp. (France).

Specimen preparation

Silane-grafted and -crosslinked POE was prepared as follows. A certain amount of POE, VTMS, DCP, and DBTL was mixed and added in a Rheocord Haake internal mixer at 170°C and 60 rpm. The residence time was 6 min. The grafted POE was then transferred to a preheated compression mold and hot pressed at 180°C under pressure of 20 MPa into sheets of 1.0 mm in thickness. Finally, the sheets were immersed in water at 85°C for 6 h, thus silane-crosslinked POE specimens were obtained.

DBTL used in the article acts as a catalyst, which can accelerate the crosslinking reaction of VTMS-grafted POE. The concentrations of DCP and DBTL used in the article remain constant (both are 0.1 phr, parts of reagent per hundred parts of POE).

Characterization

FTIR analysis

First, the grafted POE was pressed into films of about 100 μm thickness. Prior to the FTIR measurement, the films were then immersed in excessive acetone for 12 h to remove nonreacted silane and possible silane oligomers. Finally, specimens were dried in an oven under vacuum at 70°C for 8 h before test, using a Perkin-Elmer FTIR.

Differential scanning calorimetry

To study the thermal behaviors of POE before and after crosslinking, a Perkin-Elmer Paragon-1000 DSC

was used. The specimens (about 5 mg) were heated from 20 to 150°C at a scan rate of 10°C min⁻¹. The temperature was then maintained at 150°C for 3 min before cooling to 20°C at the same rate. The melting and crystallization behaviors of POE before and after crosslinking were examined. The enthalpy of fusion of 289 J g⁻¹ for 100% crystalline polyethylene was used in the calculation of percent crystallinity of POE before and after crosslinking.¹²

Gel content

Degree of crosslinking was determined by measuring gel content or insoluble fraction of silane-crosslinked POE after extraction. Weighed specimens (about 0.5 g granules, 2 cm \times 2 cm,) in a copper cage were put into boiling xylene for 24 h. After extraction, the specimens were dried in a vacuum oven at 80°C for 6 h until constant weight. The gel content was calculated using the following equation:

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

Mechanical properties

An Instron tensile tester (model 4465) was operated at a crosshead speed of 250 mm min⁻¹ using 2-kN load cell. The specimens (five samples for each specimen) were stamped cut from a 1-mm thick compression-molded sheet according to ASTM D 412.

Thermogravimetric analysis

Thermogravimetric (TG) experiments were performed using analyzer (Perkin-Elmer, TGA-7) in nitrogen atmosphere at a heating rate of 10°C min⁻¹. Weights of the samples tested were about 2 mg.

RESULTS AND DISCUSSION

Reactions of silane grafting and crosslinking

Figure 1 shows FTIR spectra of POE before (spectrum A) and after (spectra B-E) reaction with various amounts of VTMS when the extent of DCP remains constant (0.1 phr). In comparison between spectrum A and other spectra B-E, VTMS grafting onto POE is demonstrated to occur because two absorption peaks at 1092 and 1192 cm⁻¹ are assigned to the functional groups of VTMS (Si-OCH₃).

The degree of VTMS grafting POE can be determined by the gel content of crosslinked POE. The higher the degree of silane grafting, the higher the gel content. VTMS-grafted POE specimens shown earlier were then immersed in water at 85°C for 6 h, thus

TABLE I
Properties of Ethylene-Octene Copolymer
Used in This Study

Grade	Exact 0203
ρ (g cm ⁻³)	0.902
MFI (g 10 min ⁻¹)	3.0
M_w	80,000
M_w/M_n	2.9

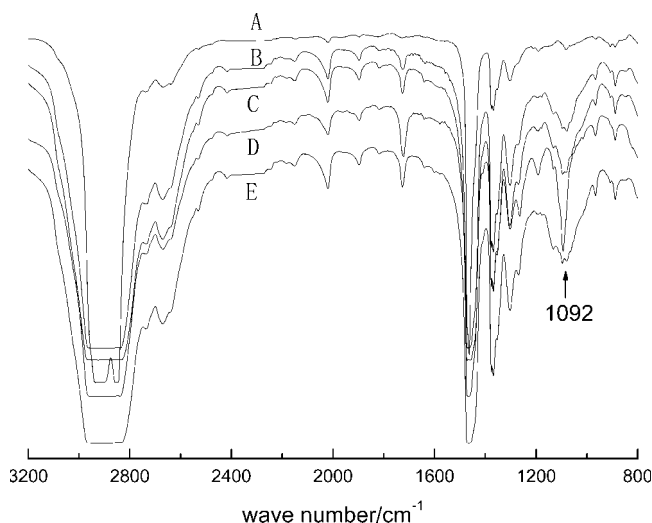


Figure 1 FTIR spectra of POE before and after silane grafting when DCP is 0.1 phr. (A) pure POE; (B) VTMS 0.5 phr; (C) VTMS 1.0 phr; (D) VTMS 1.5 phr; (E) VTMS 2.0 phr.

crosslinked POE specimens were obtained. The effects of VTMS concentration on gel content of crosslinked POE are presented in Figure 2. As can be observed from the figure, the gel content of POE increases sharply with the increase of VTMS, and levels off when the content of VTMS is over 1.0 phr. This also indicates that the degree of silane grafting of POE increases with increase of VTMS, and levels off when VTMS content reaches 0.1 phr.

Melting and crystallization behavior

DSC is a useful method for studying the thermal properties of polymeric materials, such as melting, crystallization behavior, and so on.^{13–16} In the present article, DSC measurement is carried out to evaluate

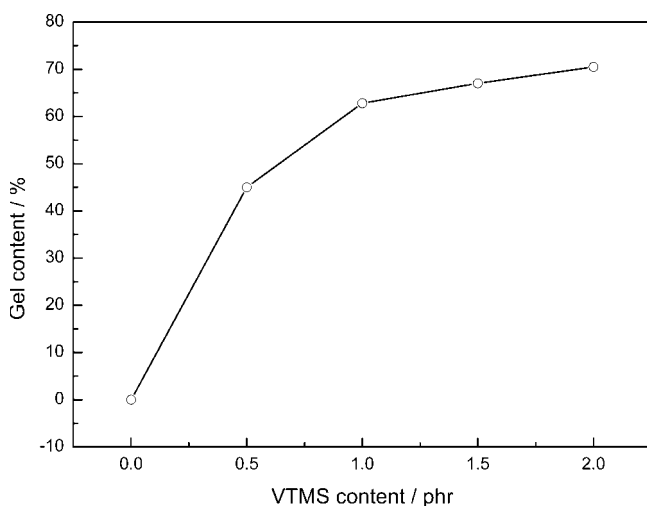


Figure 2 Effects of VTMS content on gel content of silane-crosslinked POE when DCP remains at 0.1 phr.

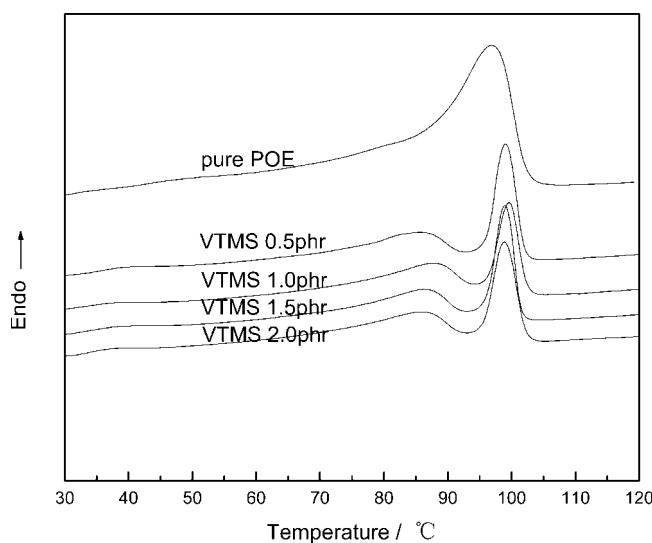


Figure 3 DSC curves of isothermal melting of silane-crosslinked POE under nitrogen (DCP remains constant, 0.1 phr).

the melting and crystallization behavior of POE before and after crosslinking.

From Figure 3 and Table II, it shows that the melting peak of POE transfers to higher temperature on addition of VTMS, owing to the crosslinking structure formed in POE, which hinders the movement of POE chains. It is also interesting to find that a single melting peak at a temperature of 94.5°C appears in DSC curve of pure POE, whereas double melting peaks occur for silane-crosslinked POE. Crosslinking generally occurs in noncrystal region for polyolefins.¹⁷ As to silane-crosslinked POE, grafting and crosslinking reaction not only hinders the crystallization, but also causes the phase separation of the two different crystals, the POE crystalline and the newly formed Si—O—Si crystalline, indicating the occurrence of multiple melting behavior of silane-crosslinked POE.

Figure 4 presents the isothermal crystallization behavior of silane-crosslinked POE at a cooling rate of 10°C min⁻¹. The exothermic peak of pure POE is at a temperature of 80.2°C, and the peak shifts to 83.9°C for silane-crosslinked POE when the content of VTMS is 0.5 phr. It is clearly seen from the figure that the

TABLE II
Effect of VTMS on the Melting and Crystallization of Silane-Crosslinked POE

VTMS (phr)	T_m (°C)	T_c (°C)	$-\Delta H_f$ (J g ⁻¹)	% X_c	% gel content
0	94.5	80.2	52.5	18.0	0
0.5	98.0	83.9	50.6	17.5	45.0
1.0	98.6	82.1	46.2	16.0	62.8
1.5	99.6	81.4	43.9	15.2	67.0
2.0	98.9	80.6	41.3	14.3	70.5

DCP remains constant, 0.1 phr.

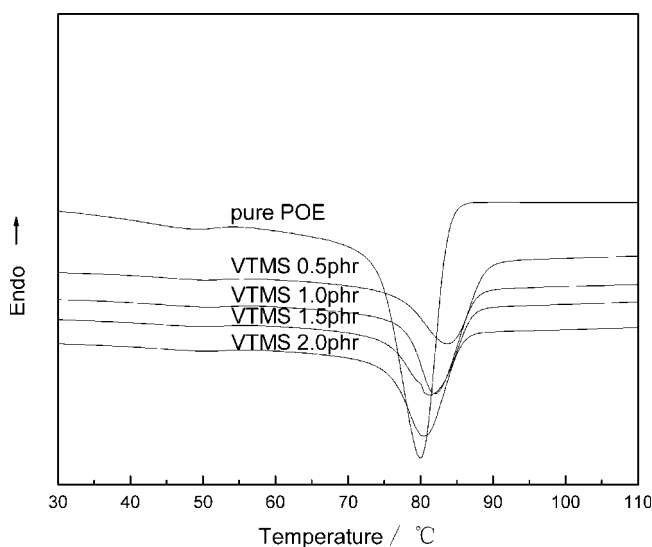


Figure 4 DSC curves of isothermal crystallization of silane-crosslinked POE under nitrogen (DCP remains constant, 0.1 phr).

peak of crystallization temperature shifts slowly to the lower value from 83.9 to 80.6°C, with the increase of VTMS from 0.5 to 2.0 phr; this is mainly due to the more restrained movement of POE chains when gel content increases, which makes the crystallization of POE more difficult.

Table II summarizes the effects of VTMS content on the degree of crystallinity (X_c) of POE, as well as on crystallization temperature, enthalpy, and gel content of POE. It can be found that degree of crystallinity of POE decreases slightly from 18.0 to 14.3% with the sharp increase of gel content from 0 to 70.5%. This can be explained as follows: VTMS used here is a organic compound with small molecule weight, and reaction of VTMS grafting onto POE has small influence on the regularity of POE chain structures, leading to the slight decrease of degree of crystallization of POE.^{18,19} Furthermore, silane crosslinking reaction of POE takes place in hot water at a temperature of 85°C, which is much lower than the melting temperature of POE, demonstrating its little influence on the degree of crystallization.

Mechanical properties

The effects of VTMS concentration on mechanical properties of silane-crosslinked POE are shown in Table III and Figure 5. As can be observed from the table and figure, tensile strength increases slowly with increase of VTMS content and reaches a maximum (28.4 MPa) when VTMS concentration is 1.5 phr, whereas a further increase of VTMS concentration results in a sharp decrease of tensile strength, e.g., from 28.4 to 20.6 MPa when the content of VTMS reaches 2.0 phr, due mainly to the excessive and non-

TABLE III
Tensile Results of Silane-Crosslinked POE When the Content of DCP Remains 0.1 phr

Silane content (phr)	Tensile strength (MPa)	Elongation at break (%)
0	16.5 (0.9) ^a	700 (10.4)
0.5	22.0 (1.1)	590 (18.0)
1	25.0 (1.0)	518 (20.0)
1.5	28.4 (0.9)	487 (18.6)
2	20.6 (1.0)	428 (19.5)

^a Values in the parentheses are standard deviations.

reacted VTMS remained in silane-crosslinked POE, which acts as a plasticizing reagent in silane-crosslinked POE, thus leading to the negative effect on tensile strength. Elongation at break of silane-crosslinked POE decreases consistently with increase of VTMS concentration, owing to the formation of silane crosslinking structure, which restricts the movement and elongation of POE chains.

Thermal stability

One of the main objectives for crosslinking polymers is to raise the upper service temperature limit of the materials or to produce the materials that are thermally stable and do not undergo melt flow even when heated above the crystalline melting point. The dynamic thermogravimetric (TG) results of pure POE and silane-crosslinked POE in nitrogen atmosphere at a heating rate of 10°C min⁻¹ are shown in Figure 6. As can be clearly seen from the figure, the temperature of 10% weight loss for pure POE (curve A) and VTMS-crosslinked POE (curves B–E) are 405, 425, 433, 443, and 452°C, respectively. The degradation temperature of silane-crosslinked POE (curves B–E) is higher than that of pure POE, demonstrating that crosslinking

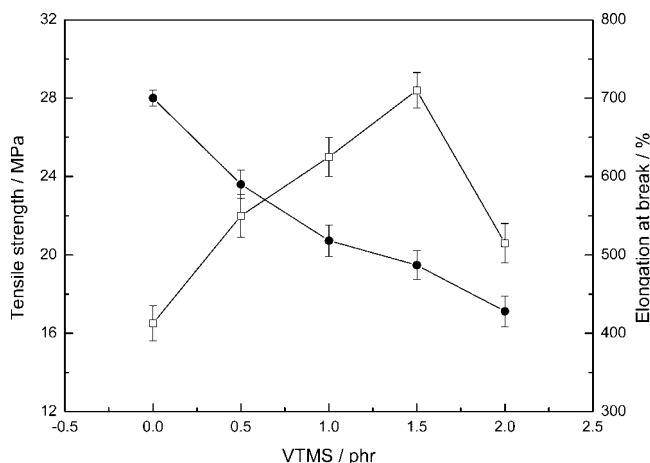


Figure 5 Effect of content of VTMS on the mechanical properties of silane-crosslinked POE when DCP remains at 0.1 phr.

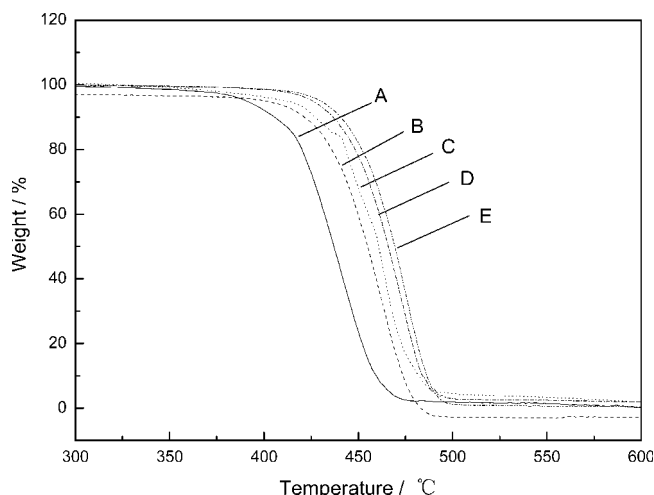


Figure 6 TG curves of VTMS-crosslinked POE when DCP remains at 0.1 phr. (A) pure POE; (B) 0.5 phr VTMS; (C) 1.0 phr VTMS; (D) 1.5 phr VTMS; (E) 2.0 phr VTMS.

structure formed in the POE help improve the thermal stability. It also shows that the thermal stability of the crosslinked POE is enhanced consistently when concentration of VTMS increases from 0 to 2.0 phr (curves B–E), due to the increase of degree of crosslinking.

CONCLUSIONS

The tensile strength of silane-crosslinked POE reaches a maximum (28.4 MPa) when the content of VTMS is 1.5 phr and concentration of DCP remains at 0.1 phr, and further addition of VTMS results in a sharp decrease of tensile strength.

Multiple melting behaviors occur for POE after silane crosslinking, and degree of crystallinity of silane-

crosslinked POE decreases slightly with increase of degree of crosslinking.

TG results demonstrate that the thermal stability of POE after crosslinking is improved than that of pure POE, and the higher the degree of crosslinking of POE, the more stable the thermal stability.

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