

Cross-Linking and Grafting with PS of EPDM in the Presence of Lewis Acids

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ABSTRACT: With Lewis Acids as catalysts in melt system, the influence of kinds of Lewis Acids, dosages of catalysts on the behaviors of crosslinking and grafting of ethylene-propylene–diene rubber (EPDM) were investigated. The Lewis Acids, such as anhydrous AlCl₃, FeCl₃, SnCl₄, could initiate the crosslinking of EPDM and the grafting between EPDM and polystyrene (PS). The carbon–carbon double bonds existing on EPDM chain were favorable to the formation of the initial carbocation in the presence of Lewis Acids. The carbocation initiated carbonium ion polymerization between the unsaturated bonds, or substituted for a proton from the phenyl in the presence of PS forming EPDM-g-PS

copolymer. Anhydrous aluminum chloride was found to be an efficient catalyst and its initiating temperatures for crosslinking or grafting were about 110°C. The amounts of gel and the data of torques showed that there was a competition between the crosslinking-grafting reaction and the degradation of blending components in the presence of AlCl₃. The EPDM-g-PS copolymer served as a compatibilizer in the EPDM/PS blends and enhanced the mechanical properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2961–2967, 2011

Key words: Lewis Acids; cationic polymerization; crosslinking; Friedel-Crafts alkylation; compatibilization

INTRODUCTION

Ethylene–propylene–diene rubber (EPDM) has been one of the fastest growing synthetic rubber both in general purpose and specialty applications since became commercialized in the 1960s. The saturated backbone structure introduces EPDMs excellent resistance to such factors as weather, ozone, and oxidation, and it could be a good alternative for substituting polybutadiene-based rubber in PS toughening.^{1–5} However, PS/EPDM blends are thermodynamically immiscible and also incompatible. The blends often give poor mechanical properties due to poor interfacial adhesion and the lack of physical and chemical interactions between different phases. Shaw and Singh^{6–8} utilized graft copolymers of EPDM with polystyrene (EPDM-g-PS), poly(styrene-co-methyl methacrylate) [EPDM-g-(PS-co-MMA)], and poly(styrene-co-maleic anhydride) [EPDM-g-(PS-co-MAH)] to prepare blends with PS/graft copolymers by mechanical mixing. Emerson Eourenceo prepared PS/EPDM

blends by *in situ* polymerization.⁹ They obtained blends with an enhancement in mechanical properties. These improvements were attributed to the compatibilization of the graft copolymers of EPDM with the polystyrene matrix, resulting in good interfacial adhesion. However, from the viewpoint of practical application, a low cost compatibilization technique would be desirable which bypasses the need for expensive additives.

In recent years, there has been considerable interest in the compatibilization of polyolefin/polystyrene in the presence of a strong Lewis acid. This approach has been thought to be a low cost *in situ* compatibilization technique which has potential in the recycling of mixed polyolefin/polystyrene wastes.^{10,11} Using AlCl₃ as an efficient catalyst, through the mechanism of Friedel-Crafts alkylation during melt blending, a number of graft copolymers, such as PE-graft-PS,^{10–15} POE-graft-PS,^{16,17} PP-graft-PS,^{18,19} have been formed. These copolymers play a role of compatibilizer at the interface of blends and reduce the interfacial tension between polymer phases. This, in turn, aids in creating and setting the ultimate morphology which then leads to an improvement in mechanical properties of the blends. Several papers^{10,16,17} reported that a competition reaction occurred between the polymer chain scission and copolymer formation during the blending process, and this method of forming graft copolymer

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did not result in undesirable crosslinking, which can occur when peroxides are used. The earlier study suggested a mechanism of Friedel-Crafts alkylation.²⁰ However, a detailed study has not been found in literature. Sun¹¹ suggested that carbon-carbon double bonds existing on polyolefin chain could be the site of carbocation formation, but no evidence was used to testify the hypothesis.

In this article, EPDM was used as a reactive substance, which has different molecule structures from PE, PP, and POE due to existing nonconjugated diene component. The behaviors of crosslinking and grafting with PS of EPDM in the presence of Lewis Acids were investigated.

EXPERIMENTAL

Materials

Polystyrene (PS, code GP525, Mw: 261,000, Mn: 116,000) was purchased from Liaoning Petrochemical, China. DSM Elastomers supplied EPDM (keltan 5508) with 2-ethylidene-5-norbornene (ENB) as diene. EPDM contains 69.0 wt % of ethylene, 26.2 wt % of propylene, and 4.8 wt % of ENB. Anhydrous aluminum chloride (AlCl₃, purity 98%), iron chloride (FeCl₃, purity 97%), tin chloride (SnCl₄, purity 99%), zinc chloride (ZnCl₂, purity 99%), were purchased from Shanghai Reagent, China. All the materials and reagents were commercial available and used without further purification.

Crosslinking and grafting

The crosslinking and grafting reaction were performed in a batch mixer (Haake Rheom IX 600 60-cm³ capacity) at 140°C under a nitrogen atmosphere. A total charge of 50 g of polymers was blended in the Haake mixer. The catalysts were dry blended with EPDM or EPDM/PS pellet mixture, these polymer/catalyst mixtures were fed into preheated Haake mixer, then blended for 8 min at 60 rpm. The torques was recorded as a function of time during blending.

Solvent extraction

The crosslinking or grafting products were extracted with xylene for 48 h to remove the linear polymer components. The residues (gel) were dried in a vacuum oven at 70°C for 24 h. The content of gel was determined using eq. (1):

$$\text{Gel(\%)} = W_1/W_0 \times 100\% \quad (1)$$

where W_0 was the weight of EPDM in the EPDM/catalyst product or in the EPDM/PS/catalyst blends, and the fraction of crosslinked material was normal-

ized to the amount of EPDM being present in the EPDM/PS/catalyst blends. W_1 was the weight of the residue after extraction.

Xylene is a good solvent for both EPDM and PS, and the extracting solution for EPDM/PS/catalyst product consisted of both homopolymers and EPDM-g-PS. The solution was distilled under vacuum to remove xylene, and the solid production was then extracted by butanone, which is a good solvent only for PS, to remove PS homopolymer (for GPC analysis). The insoluble part (EPDM and EPDM-s-PS) after butanone solvent extraction was used to FTIR analysis.

FTIR spectrometer analysis

The change of carbon-carbon double bonds absorption after reaction for EPDM/catalyst system, and the presence of PS in the residue after xylene extraction of EPDM/PS/catalyst blends and in the EPDM phase after butanone extraction of the solid production (including EPDM/PS mechanical mixture), were detected by Fourier transform IR (Nicolet-370 FTIR spectrophotometer). The residue gel samples were ground into a powder and identified using the KBr-disc method, and other samples were analyzed by film method.

DSC analysis

The EPDM or the EPDM/PS (50/50 wt %) (preblended at high temperature then cooling) mixing with catalysts were carried below 80°C. The thermal behaviors of these two mixing systems (EPDM/catalyst and EPDM/PS/catalyst) were characterized on a Perkin-Elmer DSC 7 differential scanning calorimeter using 10 mg samples, and all experiments were performed with a rate of 10°C/min.

Tensile measurement

For mechanical testing, Dog-bone shaped tensile specimens were cut from plates (about 2 mm thickness) prepared by compression molding according to GB1040-1992 (similar to ENISO 527-1994). Tensile tests were carried out on an Instron tensile tester with crosshead speed of 50 mm/min. All the tests were performed at room temperature. Results of five measurements for each sample were averaged.

Melt flow index measurement

The melt flow index (MFI) of the blends was measured using a Melt Flow Indexer according to ASTM D1238 (230°C and load of 5 kg, die $\varnothing = 2.095$ mm). After the sample was charged into the barrel within 1 min, the samples were preheated for 4 min before

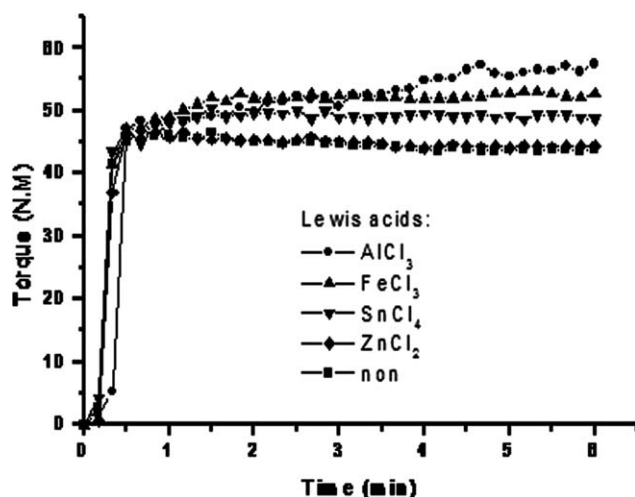


Figure 1 Torque–time curves of EPDM with different Lewis acids (0.4 wt %).

applying the load to drive the molten polymer through the die. The time interval for the cut-offs was 1–4 min depending on the flow rate of each sample.

Other characterizations

The molecular weight of homopolymer polystyrene was measured using gel permeation chromatography (GPC) equipment (Waters Associates) at room temperature. The morphologies of all blends examined here were characterized using X650 scanning electron microscope (Hitachi, Japan). Stripes of samples were immersed in liquid nitrogen for more than 15 min to cool down and then fractured immediately. The fracture surfaces were coated with Au in a vacuum chamber.

RESULTS AND DISCUSSION

Evaluation of catalyst

Four Lewis acid compounds were used as catalysts in EPDM and EPDM/PS blends, to compare their catalytic efficiency in polymer melt. The reactions were carried out in Haake batch mixer at 140°C. The various catalysts were added to EPDM or EPDM/PS (50/50 wt %) blends at 0.4 wt % content. Figure 1 shows torque–time curves of EPDM with different Lewis acids. The equilibrium torque values of different catalysts were in the order of $\text{AlCl}_3 > \text{FeCl}_3 > \text{SnCl}_4 > \text{ZnCl}_2$, and their gel contents were 72.3%, 34.4%, 20.4%, and 0%, respectively. Figure 2 shows torque–time curves of EPDM/PS blends with different Lewis acids. The equilibrium torque values of different catalyst were in the order of $\text{AlCl}_3 > \text{FeCl}_3 > \text{SnCl}_4$, and their gel contents (normalized to the amount of EPDM being present in the EPDM/PS

blends) were 105.4, 36.5, and 20.3%, respectively. It is interesting to note that significant amounts of gel had been produced under mentioned conditions. However, the values of gel were not found under same catalyst in other polymer blending systems.^{10,16,18} Their differences were attributed to the difference of molecular structure of EPDM from PE, PP, and POE, which have nonconjugated diene component. The results indicated that the unsaturated bond was ready to be attacked by Lewis Acids and form initial carbocations. These carbocations could initiate carbonium ion polymerization between the double bonds in EPDM backbone, resulting in inter or intra-cross-linking of EPDM. On the other hand, the initial carbocation can substitute for a proton from the phenyl of PS in the presence of PS, forming an EPDM-g-PS copolymer (as characterized latter). The proposed reaction mechanism is shown in Figure 3. The content of gel for EPDM/PS/ AlCl_3 (50/50/0.4 wt %) was over 100% indicating that some PS becoming the part of the gel. Among these different Lewis acids, the aluminum chloride was found to be the most efficient catalyst for the crosslinking or grafting.

Effect of catalyst content

To study the effects of catalyst contents on the crosslinking or grafting reaction, the aluminum chloride, as an efficient catalyst, was selected. The reaction was carried out in Haake batch mixer at 140°C. The catalysts were added to EPDM or EPDM/PS (50/50 wt %) blends in concentrations of 0.2, 0.4, 0.6, and 0.8 wt % of polymer, respectively. The changes of torque for EPDM and EPDM/PS blends with different catalyst concentrations were shown in Figures 4 and 5. It is interesting to note that both of these two systems have a

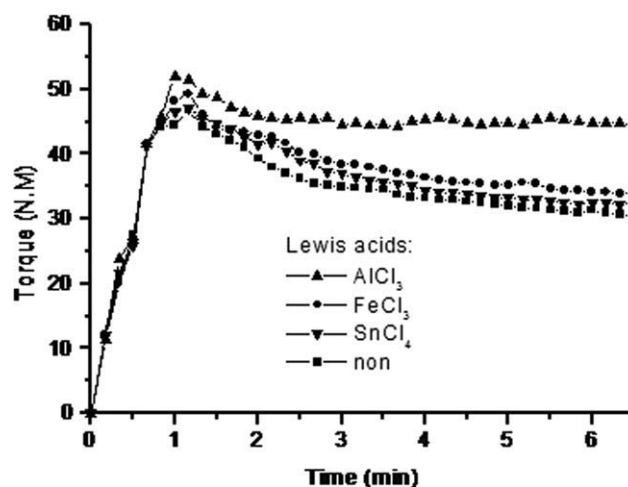


Figure 2 Torque–time curves of EPDM/PS blends with different Lewis acids (0.4 wt %).

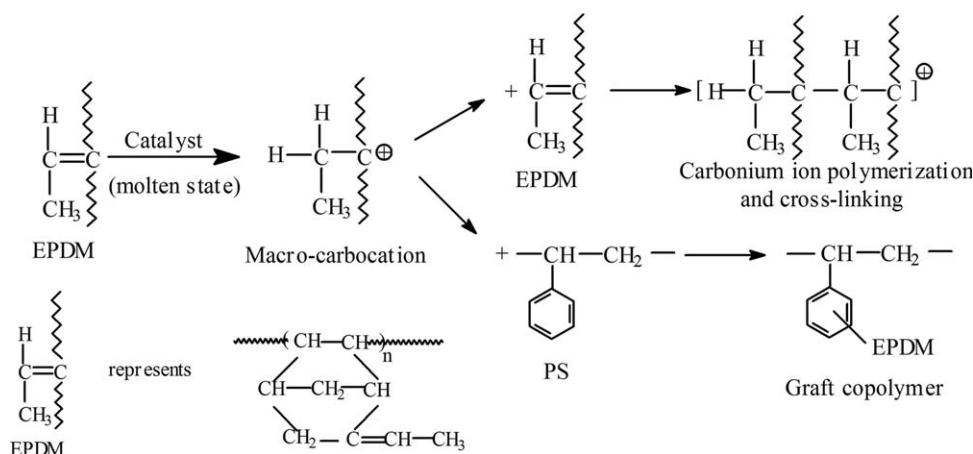


Figure 3 The proposed mechanisms of the crosslinking of EPDM and the formation of EPDM-g-PS copolymer.

peak value of the ultimate torque. This indicates an optimum catalyst concentration existed, which is in agreement with the results presented by other researchers.^{11,16,18} They concluded that this phenomena was attributed to the competition between the grafting reaction and the degradation of blending component in the presence of AlCl_3 . For these two systems, the appearance of an optimum concentration was also most likely related to the crosslinking of EPDM and the formation of EPDM-g-PS copolymer (increasing torque), and with the damage of network resulting from a chain scission or a mechanical scission and the degradation of blending component (especially PS) (decreasing torque). Such an explanation was consistent with the data shown in Table I. The optimum concentration for the two systems was about 0.4 wt %. Above the optimum concentration, the gel fraction and the torque decreased significantly (Figs. 4 and 5, Table I), this implies that the degradation of blending component become more pronounced.

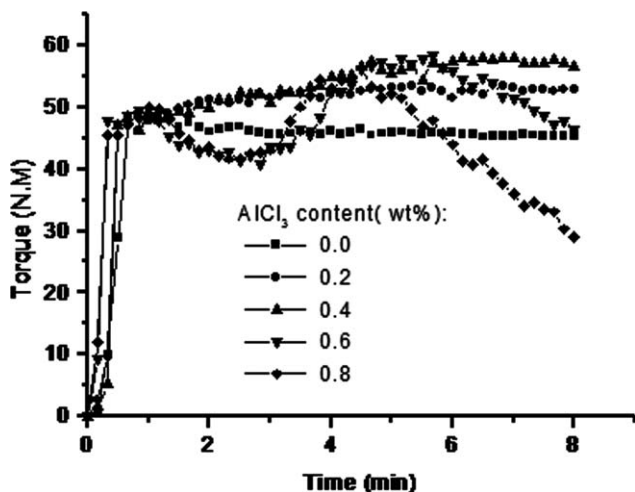


Figure 4 Torque-time curves of EPDM with different amount of AlCl_3 .

For the EPDM/PS/catalyst system, the Lewis acids attacked EPDM and formed initial carbocations, and then resulted in the crosslinking of EPDM through carbonium ion polymerization reaction and the formation of EPDM-g-PS (including EPDM-Gel-g-PS) through Friedel-Crafts alkylation reaction. From the application point of view, we hope to get more graft material than the crosslinked material. However, these two kinds of reaction all depended on the concentration of initial carbocations, that is, concentration of Lewis acids, and trends of the crosslinking and grafting caused by Lewis acids are same. So it is difficulty to get more grafting reaction than crosslinking reaction only by changing dosages of Lewis acids. Other factors (such as temperature, rotor speed, etc.) need to be further studied.

Thermal analysis

The EPDM and the PS were blended using a batch mixer at 140°C , then the resulting EPDM/PS

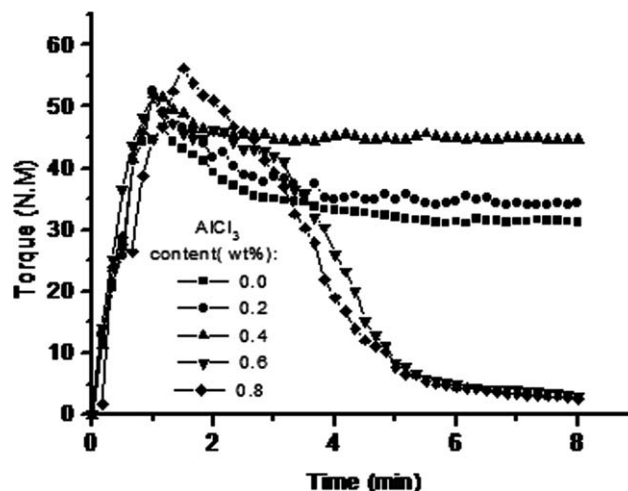


Figure 5 Torque-time curves of EPDM/PS blends with different amount of AlCl_3 .

TABLE I
The Gel Content with Different Catalyst Concentrations

Samples		Dosages of AlCl ₃ (wt %)			
		0.2	0.4	0.6	0.8
EPDM/AlCl ₃ system	Gel (%)	22.4	72.3	52.4	34.8
EPDM/PS/AlCl ₃ system	Gel (%)	33.5	105.4	34.4	6.9
	M _n of PS (×10 ⁴)	10.4 ^a	10.3	9.0	4.2

^aM_n of virgin PS.

(50/50 wt %) blends were cooled in air to room temperature. The aluminum chloride of 1 wt % was then blended with 50 g EPDM and 50 g EPDM/PS (50/50 wt %) blends in mixer at 80°C, respectively. The DSC curves of the two samples were shown in Figure 6. An exothermic reaction can be seen between 110 and 140°C in EPDM system. When the sample was carried on a vacuum oven at 120°C for 10 min, the gel content of 26% could be achieved. This implied that the cationic polymerization resulted mainly in an exothermic phenomenon. For EPDM/PS blends system, the DSC curve was in a shape of indentation starting at 110°C. This was a complex effect of cationic polymerization, glass transition of polystyrene, grafting reaction, and other chain scission reaction. One possible hypothesis can be given here to explain the phenomenon. The low-molecular weight molecules, coming from a chain scission reaction of blend component, could be devolatilized (endothermic process) at a higher temperature. Such a hypothesis was consistent with the data shown in Table I. According to the DSC curves, the temperature of the initial carbocation formation was about 110°C.

Figure 7 gives the results of DSC tests carried out on EPDM/PS (50/50 wt %) with different AlCl₃ con-

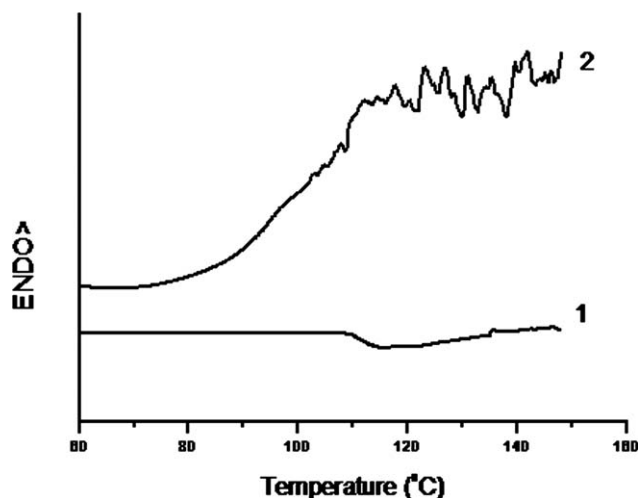


Figure 6 DSC curves of EPDM and EPDM/PS blends with catalyst (1) EPDM/AlCl₃, (2) EPDM/PS/AlCl₃.

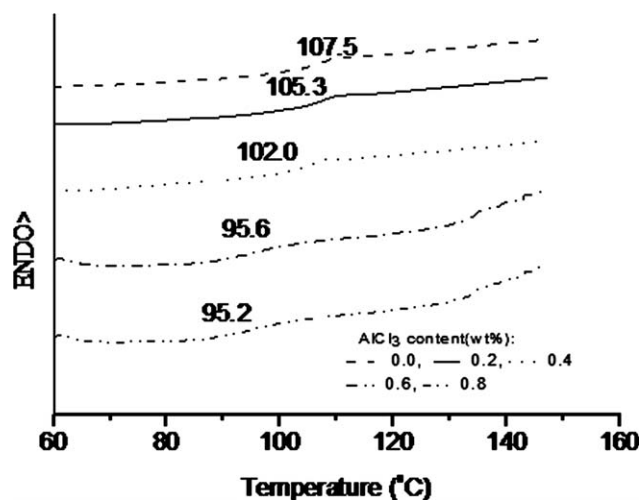


Figure 7 DSC curves of EPDM/PS blends with different AlCl₃ contents.

tents. The EPDM/PS/AlCl₃ blends exhibited lower glass transition temperatures of PS compared to that of EPDM/PS blends. The reason of these results can be explained by the plasticization effect of EPDM-g-PS copolymer. When the catalyst contents were more than 0.4%, the glass transition temperature of PS phase decreased sharply, this was due to the decreasing of the molecule weight of PS (as shown in Table I).

FTIR analysis

The double bond vibrations in EPDM were identified at 1700 and 806 cm⁻¹ in IR spectrum.²¹ The spectrum of EPDM gel produced from EPDM/AlCl₃ (0.4 wt %) system (shown in Fig. 8) showed no absorption at 1700 and 806 cm⁻¹ compared with the virgin resin. This result also confirmed that carbon-carbon double bonds existing on the EPDM chain, which can be the site of carbocation formation and

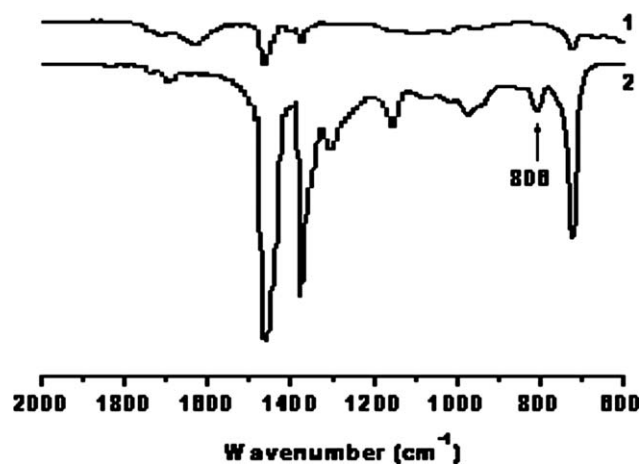


Figure 8 FTIR spectra of EPDM (1) EPDM gel, (2) EPDM.

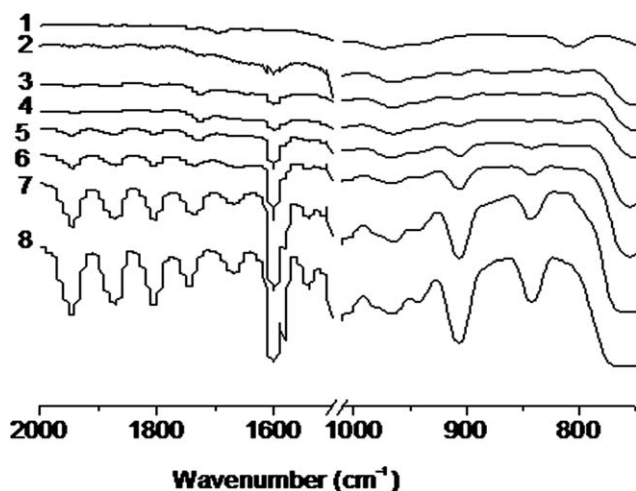


Figure 9 FTIR spectra of "EPDM" from different system: (1) EPDM from EPDM/PS system, (2) "EPDM" from EPDM/PS/SnCl₄ system, (3) "EPDM" gel from EPDM/PS/SnCl₄ system, (4) "EPDM" from EPDM/PS/FeCl₃ system, (5) "EPDM" gel from EPDM/PS/FeCl₃ system, (6) "EPDM" from EPDM/PS/AlCl₃ system, (7) "EPDM" gel from EPDM/PS/AlCl₃ system, and (8) Virgin PS.

be further polymerized. The evidence of the presence of PS in the residue (gel) after xylene extraction of EPDM/PS/catalyst blends and in the EPDM phase after butanone extraction of the solid production (including EPDM/PS mechanical mixture) were shown in Figure 9. The "EPDM" (including gel) from EPDM/PS/catalyst blend had an absorption band at 1600 cm⁻¹, which was assigned to the characteristic vibration of the phenyl group of PS. In comparison, the EPDM from EPDM/PS mechanical mixture did not have such absorption after separation. This result shows that PS could not be completely separated from EPDM/PS/catalyst blends, indicating that PS had chemically bonded to EPDM chains. The results also suggest the EPDM-g-PS copolymer was formed through a Friedel-Crafts alkylation mechanism. A comparison between the intensity of absorption of the peak at 1600 cm⁻¹ for three catalyst system showed that the AlCl₃ system had the strongest absorption among the three catalyst systems, and the FeCl₃ system had stronger absorption than that of SnCl₄ system. The result was consistent with the data shown above in Figure 2. From Figure 9, we also found that the intensity of absorption at 1700 and 806 cm⁻¹ for EPDM-g-PS reduced.

TABLE II
Effect of Dosage of AlCl₃ on the Properties of EPDM/PS Blends

Dosage of AlCl ₃ (wt%)	0	0.2	0.4	0.6	0.8
Tensile strength (MPa)	5.5	4.5	12.2	7.8	1.6
Elongation (%)	11.0	5.4	28.6	32.0	0
Melt flow ratio (g/10min)	13.0	3.5	0.7	58.8	-

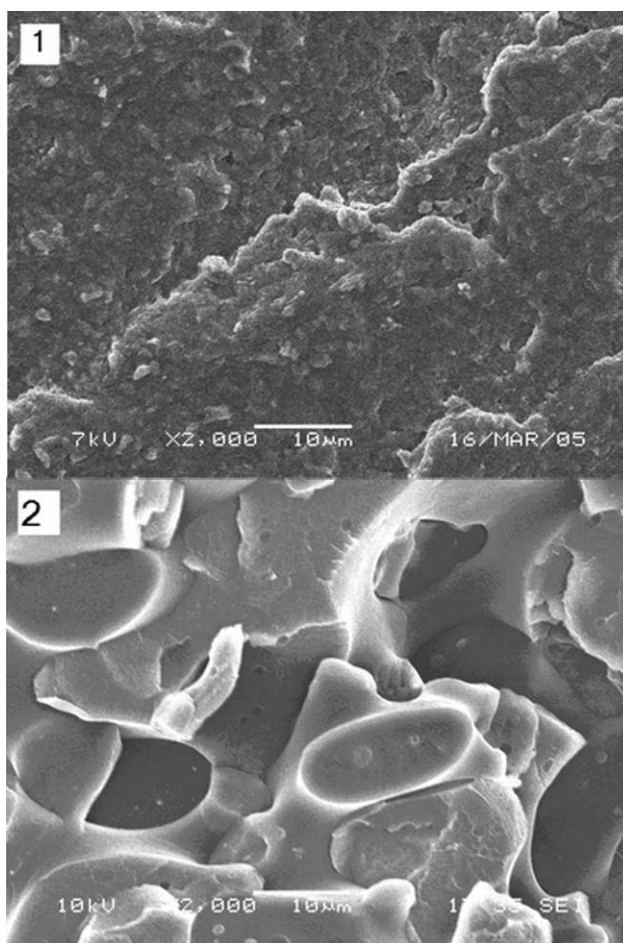


Figure 10 Scanning electron microscopic photos of EPDM/PS blends: (1) PEDM/PS/AlCl₃ = 50/50/0.4, (2) EPDM/PS = 50/50.

This further suggests that unsaturated bonds on the EPDM have the preference to form macro-carbocations in the presence of Lewis Acids catalyst, which substitutes a proton on the phenyl ring of the PS, forming a graft copolymer.

Mechanical performance of EPDM/PS blends

The EPDM/PS blends are thermodynamically immiscible and incompatible. The blends often give poor mechanical properties due to their poor interfacial adhesion and the lack of physical and chemical interactions between different phases. The EPDM-g-PS copolymer, act as a compatibilizer, which locates preferentially at the interface between PS and EPDM, reduces the interfacial tension, then leads to improvement in mechanical properties of blends.^{9,22} As above revealed, a copolymer of EPDM-g-PS can be formed during melt blending of EPDM/PS blends via a Friedel-Crafts phenyl ring alkylation of the PS. The properties of EPDM/PS (50/50 wt %) blends with different amount of AlCl₃ were shown in Table II. The mechanical properties of blends

had a peak value at the catalyst concentration of 0.4 wt %, and the MFR value was the lowest among all catalyst concentrations. The low MFR indicated an important contribution from the crosslinking and the formation of a large amount of EPDM-*g*-PS (including EPDM-Gel-*g*-PS) copolymer in the blends. As a result of the formation of EPDM-*g*-PS copolymer, the mechanical properties of EPDM/PS blends were improved considerably. A coarser morphology was obtained in this blend, when compared to the morphology of the same blend without catalyst (Fig. 10). Morphology coarsening was caused by crosslinking of the rubber phase.²² When the amount of catalyst was 0.2 wt %, the mechanical properties were lower than that of noncatalyst systems, the reason can be explained by the crosslinking of EPDM and few formation of copolymer. The properties of EPDM/PS blend decreased significantly at higher catalyst concentration due to the degradation of the blend components. This is consistent with earlier studies.^{11,17,18}

CONCLUSIONS

The crosslinking of EPDM and the grafting between EPDM and PS were achieved using Lewis Acids as catalyst in a melt blending process. The aluminum chloride was an efficient catalyst for the initial carbocation formation. The initial carbocation initiated carbonium ion polymerization between the unsaturated bonds among EPDM backbone, and substituted for a proton from the phenyl ring in the presence of PS forming EPDM-*g*-PS (including EPDM-Gel-*g*-PS) copolymer. The amount of gel and the data of torque showed a competition between the crosslinking-graft-

ing reaction and the degradation of blending components in the presence of AlCl₃. The mechanical characterization of EPDM/PS blends showed a significant improvement in an optimum catalyst concentration.

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