

Studies on Mechanical and Morphological Behavior of Hybrid Nanoclay-Reinforced EPDM-g-TMEVS/PS Blends

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ABSTRACT: A new copolymer of tris(2-methoxyethoxy) vinylsilane (TMEVS)-grafted ethylene-propylene-diene elastomer (EPDM-g-TMEVS) has been developed by grafting of TMEVS onto EPDM by using dicumylperoxide (DCP) initiator. The linear polystyrene blends (EPDM-g-TMEVS/PS) based on EPDM-g-TMEVS have been synthesized with varying weight percentages of polystyrene in a twin-screw extruder. In a similar manner, the dynamically vulcanized and nanoclay-reinforced polystyrene blends have also been developed using DCP and organically modified montmorillonite clay separately by means of a twin-screw extruder. The grafting of TMEVS onto EPDM at allylic position present in the third monomer of EPDM has been confirmed by Fourier Transform infrared spectroscopy. The effect of silane-grafted EPDM and concentration of nanoclay on mechanical properties of polystyrene blends has been studied as per ASTM standards. The morphological behavior of these blends has been investigated

using scanning electron microscope. It was observed that the incorporation of silane-grafted EPDM enhanced the impact strength and the percentage elongation of linear and dynamically vulcanized blends. However, the values of tensile strength, flexural strength, flexural modulus, and hardness of the blends were found to be decreasing with the increase of silane-grafted EPDM. In the case of nanoclay-reinforced polystyrene blends, the values of impact strength, tensile strength, flexural strength, flexural modulus, and hardness were increased with an increase in the concentration of nanoclay. XRD studies have been carried out to confirm the formation of nanoclay-reinforced EPDM-g-TMEVS/PS blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2859–2871, 2009

Key words: graft copolymer; EPDM-g-TMEVS; EPDM-g-TMEVS/PS; nanoclay-reinforced blends; mechanical properties; XRD studies

INTRODUCTION

The main objective of rubber toughening of brittle polymer such as polystyrene by the elastomeric particles is to improve interfacial adhesion, rubber particle dispersion, and stress transfer between the phases to provide a good balance of properties. The incorporation of dispersed elastomeric particles in a rigid polymer matrix has attracted considerable attention because of its industrial importance, among other types of polymer blends.^{1–5} Liu and Baker studied the effects of rubber particle size and rubber/matrix adhesion on the impact properties of a brittle polymer. It has been proved that the interfacial adhesion between the rubber phase and the PS matrix is reducing the rubber particle size and also plays a further role in improving the impact properties of the matrix polymer.⁶ The essential characteristics of rubber toughening is that the

improvement of impact resistance of the parent rigid polymer.^{7–9} Most of the polymer pairs are immiscible and incompatible. These incompatible blends often give poor mechanical properties because of poor interfacial adhesion and the lack of physical and chemical interactions between different phases. Even though most of the polymer blends are incompatible, many may be made compatible by several methods.^{10,11} Compatibility of such blends can be enhanced by the addition of an appropriate presynthesized block or graft copolymers.¹² The addition of a small amount of graft or block copolymer to an immiscible polymer blend is often a powerful means to increase the interaction between the phases and thus enhanced the mechanical properties because of the formation of a strong interface.^{13,14} Lourenco and Felisberti investigated the thermal and mechanical properties of *in situ* polymerized PS/EPDM and reported that the mechanical properties of the blends are influenced by the increase in the average size of EPDM domains with the increase in the polymerization temperature and EPDM content.¹⁵ Crevecoeur et al. have studied the effect of poly(styrene/ethylene-propylene) (SEP) compatibilizer on impact strength of polystyrene/EPDM blends and found

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that the impact strength of PS/EPDM blend was increased because of the enhanced adhesion between the dispersed EPDM phase and the polystyrene matrix.¹⁶ Hrnjak-Murgic and coworkers studied the effect of structure of ethylene-propylene-diene-graft-polystyrene-graft copolymers on morphology and mechanical properties of SAN/EPDM blends and reported that the structures of copolymers influence the miscibility of the blends and enhanced the mechanical properties.¹⁷ Singh and Shaw have studied the compatibility of polystyrene/EPDM blends based on graft polyblends and found that the compatibility between polystyrene and EPDM was enhanced by incorporation of compatibilizer such as styrene-grafted EPDM, styrene-methylmethacrylate-grafted EPDM, and styrene-maleic anhydride-grafted EPDM.^{18–20} Ramar and Alagar have studied the effect of grafting of tris(2-methoxyethoxy) vinylsilane (TMEVS) onto EPDM and reported that the grafting efficiency reached a maximum at 6 wt % by weight of TMEVS.²¹ Modified rubbers have also been used as impact modifier for brittle polystyrene and polyvinylchloride.²² EPDM is chosen as dispersed phase in this study for rigid and brittle polystyrene because of its excellent weathering properties than the other conventional rubbers like butadiene and isoprene, and it has saturated ethylene and propylene backbone and unsaturated side chain such as 2-ethylidene-5-norbornene, which provide crosslinking.^{23–25} Nanohybrid materials, on the other hand, exhibiting outstanding improvement in tensile/flexural properties, barrier properties, thermal stability, and glass transition temperature even at very low concentration, is chosen as filler for this study.^{26–31} Yan and coworkers studied mechanical and dynamic mechanical properties of nylon 6, 6/montmorillonite nanocomposites and reported that the effect of organic MMT loading clearly increased Young's modulus and tensile strength. However, it decreased ductility and fracture toughness of nylon 6, 6.³² Kausch and Michler studied the effect of nanoparticle size and size distribution on mechanical behavior of filled amorphous thermoplastics polymers and reported that the uniform dispersion of nanoparticles in the thermoplastic polymers enhances the toughness.³³ Choi et al. have studied the effect of nanoclay on polystyrene/montmorillonite nanocomposites and found that the intercalation of nanoclay in the polystyrene matrix is increased the mechanical properties.³⁴ Usuki et al. have found that the values of tensile strength and storage modulus of the hybrid EPDM-clay composite were higher than that of the virgin EPDM and also reported that the gas permeability of EPDM-clay hybrid was decreased to 30% when compared with that of virgin EPDM.³⁵ Wills et al. investigated the morphology and impact properties of polystyrene-maleic anhy-

dride/bromobutyl rubber blends and found that dimethylaminoethanol serves as a reactive compatibilizing agent for these blends, which increase fivefold reductions in the size of the disperse phase because of this effect impact strength of the blend increases.³⁶ Chang and coworkers investigated the rubber-toughened poly(trimethylene terephthalate)-organoclay nanocomposites and reported that the nanoparticles induced a reduction of rubber particle size in the matrix and enhances the stiffness of nanocomposites without adversely affecting its toughness.³⁷

With the above reviews, in this investigation, an attempt has been made to develop linear, dynamically vulcanized, and nanoclay-reinforced EPDM-g-TMEVS/PS blends in a twin-screw extruder by using dicumylperoxide (DCP) as initiator and graft copolymer of TMEVS-grafted ethylene-propylene-diene terpolymer (EPDM-g-TMEVS) as dispersed phase. The effects of incorporation of EPDM-g-TMEVS copolymer and nanoclay concentration on mechanical properties such as impact strength, tensile strength, flexural strength, percentage elongation, flexural modulus, and hardness were studied. The morphological behavior was investigated by means of scanning electron microscope (SEM). XRD studies were carried out to confirm the formation of nanoclay-reinforced polystyrene blends and the results are discussed by comparing with those of virgin polystyrene.

EXPERIMENTAL

Materials

Ethylene-propylene-diene terpolymer (Nordal IP 4770R) with Mooney viscosity 70 ML₁₊₄ at 125°C procured from DuPont Dow elastomers, USA. Polystyrene obtained from Supreme Petrochemicals, India. These materials were used after proper drying. Dicumylperoxide (99.8% assay) obtained from Lancaster, U.K. and tris(2-methoxyethoxy) vinylsilane (TMEVS) was procured from Aldrich, USA. These materials were used as received.

Modification of montmorillonite clay

The montmorillonite clay was organically modified by using cetyl ammonium bromide following the procedure reported elsewhere^{38,39} to utilize them for the development of nanocomposites using EPDM-g-TMEVS and polystyrene matrix.

Preparation of EPDM-g-TMEVS

The grafting of TMEVS on to EPDM was carried out in the presence of 0.1 wt % DCP at 170°C for 6 min

with the screw rotation speed of 60 rpm. The extrudate after cooling was passed through a cutter to be chipped into granules. The EPDM-g-TMEVS granules obtained were dried at 60°C for 2 h before the preparation of blend.

Preparation of EPDM-g-TMEVS/PS blends

The blends of EPDM-g-TMEVS/PS with different composition were prepared by melt mixing in the twin-screw extruder (Berstorff) at 190°C in the presence and absence of 1 wt % DCP initiator and 0.01 wt % dibutyltindilaurate catalyst for 6 min with the screw rotation speed of 100 rpm. Linear EPDM-g-TMEVS/PS blends obtained in the absence of DCP and dynamically vulcanized EPDM-g-TMEVS/PS blends obtained by mixing polymers initially at molten state for 4 min and DCP was added and processed for another 2 min.

Preparation of nanoclay-reinforced EPDM-g-TMEVS/PS blends

The nanoclay-reinforced polystyrene blends were prepared with varying percentages (2 and 4 wt %) of organically modified montmorillonite clay. During the preparation of reinforced polystyrene blends, the polymers were mixed in a molten state for 3 min and nanoclay was added, again mixing was carried out continuously at 190°C for another 1 min, followed by the addition of DCP over a period of 1 min. The extrudate was cooled and passed into cutter to be chipped into granules of blends.

Preparation of specimen

The specimens were prepared by injection molding (WIDSOR SP130). The blends prepared by melt mixing in the twin-screw extruder were dried in a hot air oven at 80°C for 2 h. The molding was carried out at 200°C with a pressure of 5 MPa in the injection-molding machine. The specimens were removed from the mold after allowing the mold to attain room temperature. The test specimens for various tests were obtained using appropriate mold as per ASTM standards.

FTIR spectral analysis

The grafting of TMEVS onto EPDM and blending of EPDM-g-TMEVS with polystyrene were confirmed by Fourier Transform infrared spectroscopy (FTIR) (Shimadzu 8300, Kyoto, Japan) spectra. FTIR spectra of pure EPDM, EPDM-g-TMEVS, EPDM-g-TMEVS/PS blend, and polystyrene were obtained by using granules, and spectra of TMEVS were recorded using liquid sample.

Mechanical properties

Izod impact strength

The notched Izod impact strength of the sample was tested as per ASTM D 256-88. All the samples were notched and tested, so that they would be more sensitive to the transition between ductility and brittleness. Specimens having thickness 3 mm width, 10 mm cross section, and 64 mm length were clamped in the base of the pendulum-testing machine. The pendulum was released and the force consumed in breaking the sample calculated from the height of the pendulums reached.

Tensile and flexural properties

Tensile strength and flexural properties were measured using a tensile tester following the standard procedure described as per ASTM D 638 and D 790 at a crosshead speed of 5 mm/min.

Hardness (Shore-D)

The hardness of the sample was measured using Shore-D durometer according to ASTM D422 with sample of 50 mm by 50 mm square cross section having thickness of 6 mm was used.

SEM analysis

The morphological texture of the blend was observed by scanning electron microscopy (JEOL JSM-6360, Japan). SEM micrographs were taken from cryogenically fractured molded tensile specimens. The fractured surfaces were sputtered with gold before viewing.

XRD analysis

The XRD is one of the most valuable methods to characterize the structure of polymer-clay nanocomposites. The X-ray diffraction technique is the most direct and simple method to evaluate the spacing between the clay layers. The experimental 2θ value is the angle between the diffracted and incoming X-ray waves. The nanoclay-reinforced blend samples were analyzed using a Rich Scifert XRD analyzer (Model 3000, Almelo, Netherlands).

RESULTS AND DISCUSSION

FTIR analysis

The Figure 1(a) represents the IR spectrum of EPDM. It shows the $-\text{CH}_2$ wagging vibration at 750 cm^{-1} may be because of the presence of polyethylene chain. The unsaturation band ($>\text{C}=\text{CH}-$) at

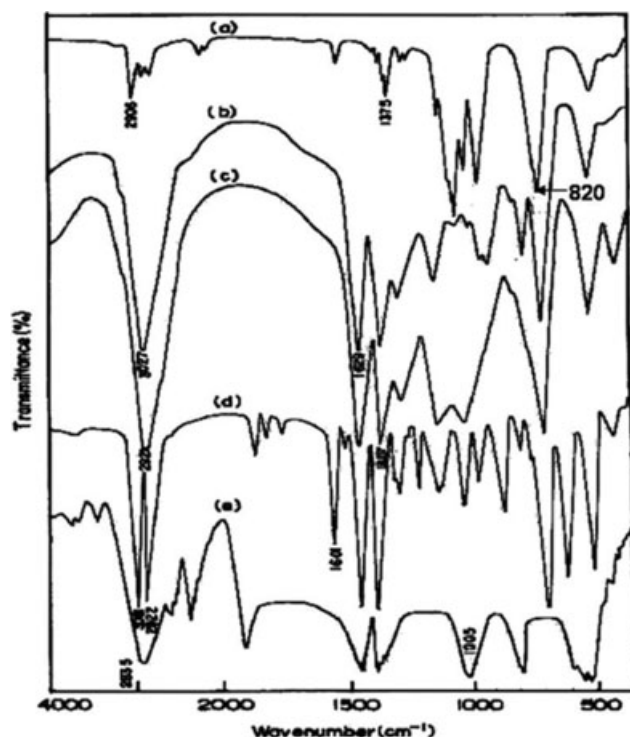


Figure 1 FTIR spectrum of (a) EPDM, (b) TMEVS, (c) EPDM-g-TMEVS, (d) polystyrene, and (e) EPDM-g-TMEVS/PS.

820 cm^{-1} is due to the presence of 2-ethylidene-5-norbornene content. The $-\text{CH}_3$ symmetric bending vibration at 1375 cm^{-1} because of the presence of propylene group, $-\text{CH}_2$ rocking vibration at 1461 cm^{-1} , the C–C stretching vibration at 2854 cm^{-1} , C–H stretching vibration (aliphatic) at 2906 cm^{-1} . Figure 1(b) presents the IR spectrum of TMEVS. It shows the Si–CH=CH₂ at 875 cm^{-1} , Si–O stretching vibration at 1025 cm^{-1} , C=C stretching vibration at 1629 cm^{-1} , and C–H stretching vibration (vinyl) at 3027 cm^{-1} , respectively. Figure 1(c) presents the IR spectrum of EPDM-g-TMEVS, which indicates $-\text{CH}_2$ rocking vibration at 1350 cm^{-1} , $-\text{CH}_3$ sym-

metric bending vibration at 1407 cm^{-1} , and C–H stretching vibration at 2921 cm^{-1} . However, $-\text{CH}_2$ wagging vibration of Si–CH=CH₂ at 875 cm^{-1} , C=C stretching at 1629 cm^{-1} , and C–H stretching vibration (vinyl) at 3027 cm^{-1} were found disappeared because of grafting of TMEVS with unsaturation present in the side chains of ENB monomer at 820 cm^{-1} without affecting the Si–O stretching vibration at 1025 cm^{-1} . The absence of peaks at 820, 875, and at 3027 cm^{-1} indicates that $>\text{C}=\text{CH}-$ is utilized for new chemical bond formation with TMEVS. Figure 1(d) presents the IR spectrum of polystyrene. It shows that the $-\text{CH}_2-\text{CH}_2-$ wagging vibration at 757 cm^{-1} because of the presence of polyethylene backbone, $-\text{CH}_2$ rocking vibration at 1493 cm^{-1} , $-\text{C}=\text{C}$ stretching because of phenyl group at 1601 cm^{-1} , the C–H stretching vibration (aliphatic) at 2922 cm^{-1} , and $-\text{C}-\text{H}$ stretching vibration (aromatic) at 3081 cm^{-1} . Figure 1(e) represents the IR spectrum of EPDM-g-TMEVS/PS blends. The $-\text{CH}_2$ wagging vibration at 757 cm^{-1} , Si–O stretching vibration at 1005 cm^{-1} , $-\text{CH}_3$ symmetric vibration at 1375 cm^{-1} , $-\text{CH}_2$ rocking vibration at 1461 cm^{-1} , and C–H stretching vibration (aliphatic) at 2835 cm^{-1} . The formation of Si–O stretching vibration at 1005 cm^{-1} confirms the formation of $-\text{Si}-\text{O}-\text{Si}-$ linkage in the blends.

Mechanical properties of linear EPDM-g-TMEVS/PS blends

The values of mechanical properties such as impact strength, tensile strength, elongation at break, flexural strength, and flexural modulus of linear blends are presented in Table I and Figures 2–6.

Impact strength

The values of impact strength (Table I) of linear EPDM-g-TMEVS/PS blends are increased with

TABLE I
Mechanical Properties of Linear EPDM-g-TMEVS/PS blends

Composition	Izod impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)
EV ₅ PS ₉₅	81.0 ± 2	43 ± 3	3.5 ± 1	74.0 ± 3	2312 ± 24
EV _{7.5} PS _{92.5}	94.0 ± 6	40 ± 4	4.1 ± 5	69.0 ± 5	2024 ± 35
EV ₁₀ PS ₉₀	127.0 ± 5	38 ± 9	5.4 ± 4	65.0 ± 3	1900 ± 25
EV ₁₅ PS ₈₅	109.4 ± 8	32 ± 6	7.2 ± 5	59.1 ± 9	1843 ± 27
EV ₂₀ PS ₈₀	88.0 ± 5	28 ± 2	8.0 ± 7	54.3 ± 5	1670 ± 30
EV ₃₀ PS ₇₀	75.0 ± 3	25 ± 8	9.3 ± 3	51.0 ± 2	1600 ± 18
EV ₅₀ PS ₅₀	72.0 ± 8	24 ± 3	10.4 ± 2	49.2 ± 9	1540 ± 21
PS ₁₀₀	20.0 ± 7	49 ± 4	2 ± 3	82.0 ± 4	2700 ± 28

PS, wt % of polystyrene; EV, wt % of EPDM-g-TMEVS copolymer.

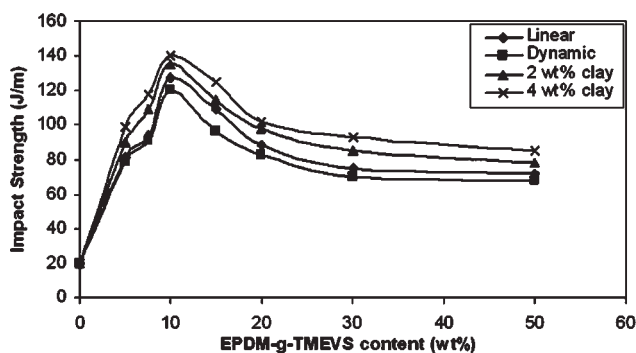


Figure 2 Effect of EPDM-g-TMEVS content on impact strength of polystyrene blends. (a) Linear EPDM-g-TMEVS/PS blends, (b) dynamically vulcanized EPDM-g-TMEVS/PS blends, (c) 2 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends, and (d) 4 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends.

increasing percentage incorporation of silane-grafted EPDM in the polystyrene matrix when compared with that of neat polystyrene. However, the impact strength values of polystyrene blends consisting of rubber content up to 10 wt % are higher than that of the blends consisting of above 10 wt % of rubber. This trend can be explained due to the fact that the presence of small portion of rubber domains in the matrix and dispersed uniformly in the matrix, which result in reduction of rubber particle size (1 μm) and followed by the prevention of coalescence. It increases the interphase adhesion between the blend constituents, which result in enhancement in the value of impact strength. When increase the content of rubber in the matrix (above 10 wt %), the values of impact strength decreased because of the weakening of interphase adhesion between the matrix and rubber, which resulted in increase of rubber particle size. For example, when 5, 7.5, 10, 15, 20, 30, and 50 wt % of EPDM-g-TMEVS incorporated into polystyrene matrix, the values of impact strength were

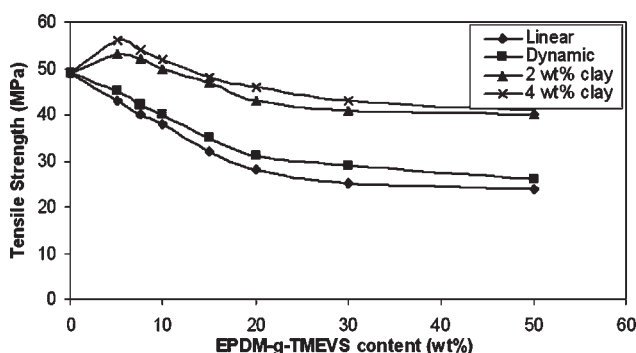


Figure 3 Effect of EPDM-g-TMEVS content on tensile strength of polystyrene blends. (a) Linear EPDM-g-TMEVS/PS blends, (b) dynamically vulcanized EPDM-g-TMEVS/PS blends, (c) 2 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends, and (d) 4 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends.

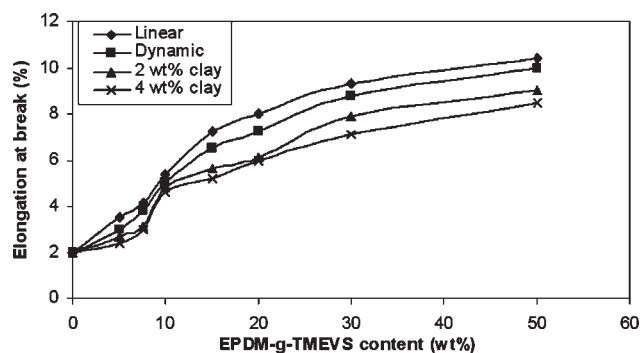


Figure 4 Effect of EPDM-g-TMEVS content on elongation at break polystyrene blends. (a) 4 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends, (b) 2 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends, (c) dynamically vulcanized EPDM-g-TMEVS/PS blends, and (d) linear EPDM-g-TMEVS/PS blends.

increased by 4.05, 4.70, 6.35, 5.5, 4.4, 3.8, and 3.6 times, respectively, when compared with the value of unmodified polystyrene [Fig. 2(a)].

Tensile strength and percentage elongation

The values of tensile strength (Table I) of the linear EPDM-g-TMEVS/PS blends were decreased with increasing percentage incorporation of EPDM-g-TMEVS in the polystyrene matrix when compared with the value of unmodified polystyrene. The incorporation of dispersed phase into the matrix makes the blends flexible because of cocontinuity of rubbery phase, which increase the flow and impart sufficient mobility of the chain segments of the blend, it occurs at a molecular level. The decrease in the value of tensile strength with increasing elastomer content is expected and reported for toughening of rigid polymers⁷. The values of tensile strength of EV₅PS₉₅, EV_{7.5}PS_{92.5}, EV₁₀PS₉₀, EV₁₅PS₈₅, EV₂₀PS₈₀, EV₃₀PS₇₀, and EV₅₀PS₅₀ blends were decreased to 12,

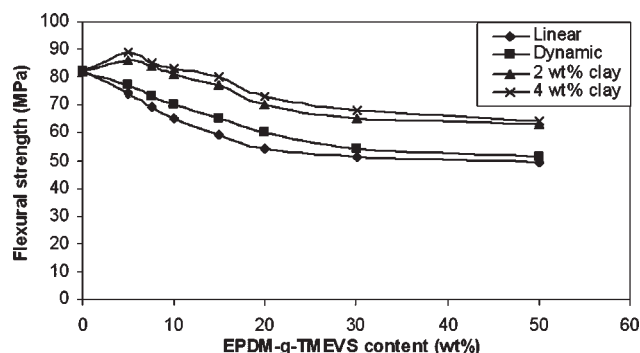


Figure 5 Effect of EPDM-g-TMEVS content on flexural strength of polystyrene blends. (a) Linear EPDM-g-TMEVS/PS blends, (b) dynamically vulcanized EPDM-g-TMEVS/PS blends, (c) 2 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends, and (d) 4 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends.

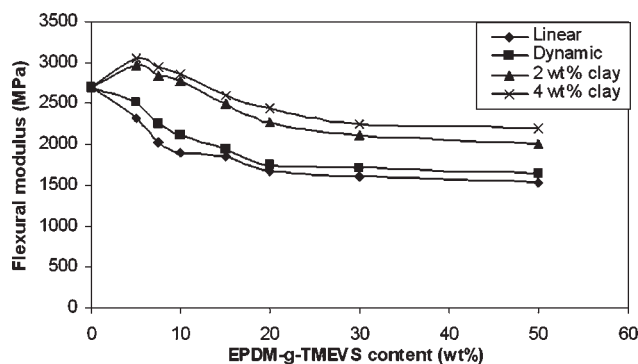


Figure 6 Effect of EPDM-g-TMEVS content on flexural modulus of polystyrene blends. (a) Linear EPDM-g-TMEVS/PS blends, (b) dynamically vulcanized EPDM-g-TMEVS/PS blends, (c) 2 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends, and (d) 4 wt % nanoclay-reinforced EPDM-g-TMEVS/PS blends.

18, 22, 34, 42, 48.9, and 51%, respectively. It may also be explained by the synergistic effect of the blends, which changes the mechanical behavior of polystyrene matrix by increase in the average size of the rubber domains. However, the percentage elongation of linear EPDM-g-TMEVS/PS blends is increased with increasing the incorporation of silane-grafted EPDM into the matrix. This is the fact that the enhancement of polymer chain mobility is due to rubbery domains and results an increase in the values of elongation at break. For example, the values are increased by 75, 105, 170, 260, 300, 350, and 420%, respectively, with the incorporation of varying percentage concentration of silane-grafted EPDM namely 5, 7.5, 10, 15, 20, 30, and 50% into the polystyrene matrix [Figs. 3(a) and 4(d)].

Flexural properties

The flexural properties (Table I) such as flexural strength and flexural modulus of linear EPDM-g-

TMEVS/PS blends were decreased by the addition of varying percentage concentration of silane-grafted EPDM in the polystyrene matrix. This may be explained because of lowering of brittle behavior and in turn reduce the stiffness of polystyrene matrix (catastrophic effect) and improving ductile behavior of the blend because of the presence of rubbery phase. Similar effect was observed on the values of flexural modulus. The decrease in the values of modulus with increasing elastomer content is expected and reported for toughening of rigid polymers (7). For example, the incorporation of 5, 7.5, 10, 15, 20, 30, and 50% of silane-grafted EPDM decreased the values of flexural strength of polystyrene blends by 9.7, 15.8, 20.7, 28, 34.1, 37.8, and 40%, respectively, when compared with that of unmodified polystyrene [Table I and Figs. 5(a) and 6(a)].

Mechanical properties of dynamically vulcanized EPDM-g-TMEVS/PS blends

The values of impact strength, tensile strength, percentage elongation at break, flexural strength, and flexural modulus of dynamically vulcanized blends are presented in Table II and Figures 2–6.

Impact strength

The values of impact strength of dynamically vulcanized EPDM-g-TMEVS/PS blends increased with increase in the percentage incorporation of silane-grafted EPDM into polystyrene matrix [Fig. 2(b)]. It may be explained because of the grafting of EPDM-g-TMEVS onto polystyrene by dynamic vulcanization using radical initiator, which in turn enhanced the intercrosslinking between the rubbery phase and plastic phase and thus improved the values of impact strength. However, when compared with the values of linear blends (Table I), the dynamically vulcanized EPDM-g-TMEVS/PS blends possess lower values of impact strength (Table II). It may be

TABLE II
Mechanical Properties of Dynamically Vulcanized EPDM-g-TMEVS/PS Blends

Composition	Izod impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)
EV ₅ PS ₉₅	78.5 ± 2	45 ± 3	3.0 ± 4	77 ± 4	2500 ± 30
EV _{7.5} PS _{92.5}	90.8 ± 6	42 ± 1	3.8 ± 8	73 ± 7	2250 ± 28
EV ₁₀ PS ₉₀	120.0 ± 4	40 ± 6	5.0 ± 5	70 ± 3	2115 ± 25
EV ₁₅ PS ₈₅	96.0 ± 1	35 ± 6	6.5 ± 3	65 ± 5	1940 ± 32
EV ₂₀ PS ₈₀	82.5 ± 3	31 ± 8	7.2 ± 4	60 ± 3	1750 ± 26
EV ₃₀ PS ₇₀	70.0 ± 3	29 ± 3	8.8 ± 7	54 ± 2	1715 ± 40
EV ₅₀ PS ₅₀	68.0 ± 4	26 ± 1	10.0 ± 9	51 ± 7	1640 ± 18
PS ₁₀₀	20.0 ± 5	49 ± 5	2 ± 3	82 ± 4	2700 ± 27

PS, wt % of polystyrene; EV, wt % of EPDM-g-TMEVS copolymer.

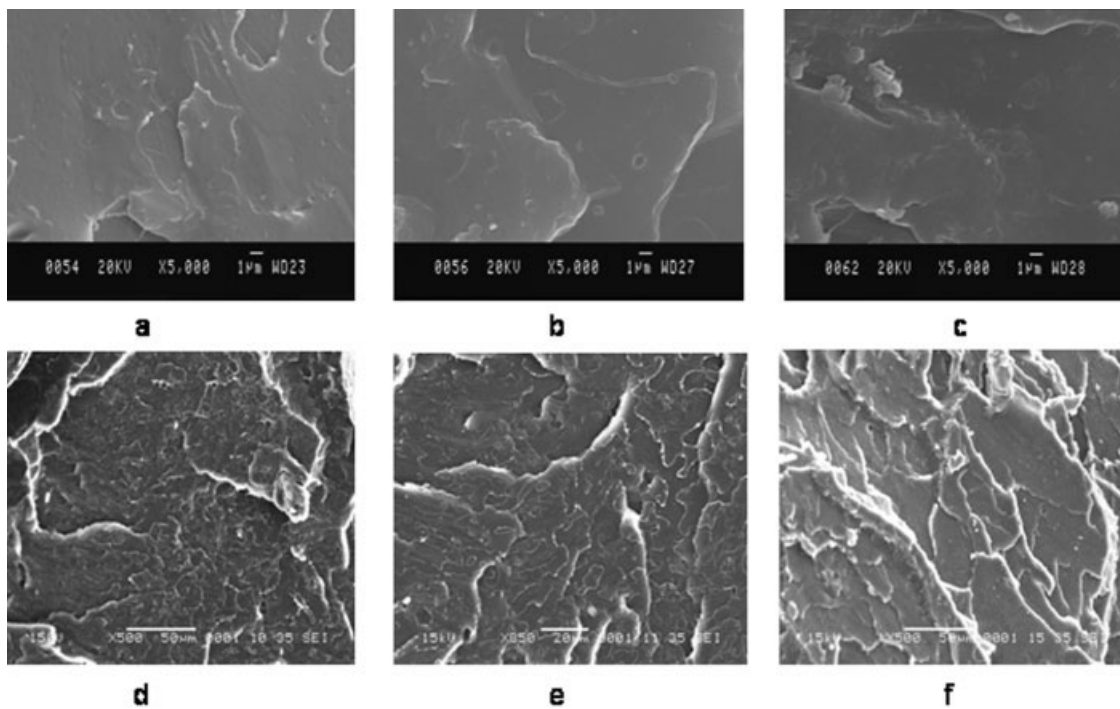


Figure 7 SEM micrographs of linear polystyrene blends (a) EV₅PS₉₅, (b) EV_{7.5}PS_{92.5}, (c) EV₁₀PS₉₀, (d) EV₂₀PS₈₀, (e) EV₃₀PS₇₀, and (f) EV₅₀PS₅₀.

due to improved crosslinking imparted by peroxide curing, which results in an enhanced resistance to void formation in the rubbery constituent of the blends. The polystyrene blends consisting of silane-

grafted EPDM namely 5, 7.5, 10 wt %, 15, 20, 30, and 50% increased the values of impact strength by 4.0, 4.5, 6.0, 4.8, 4.1, 3.5, and 3.3 times, respectively, when compared with the value of unmodified

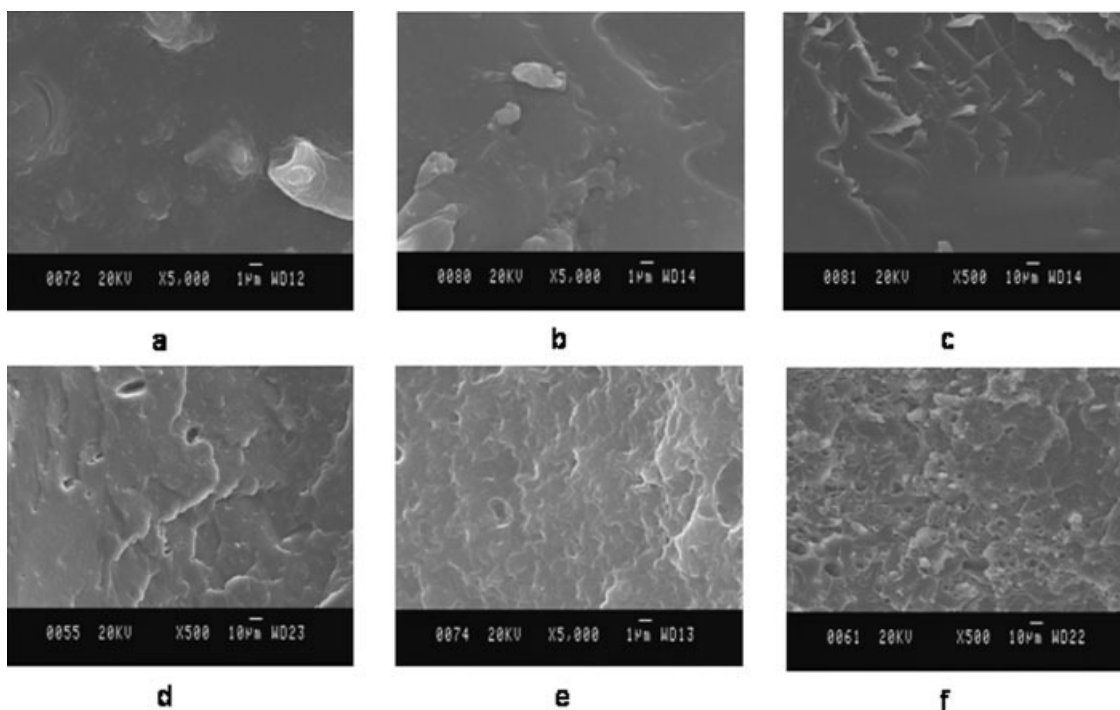


Figure 8 SEM micrographs of dynamically vulcanized polystyrene blends (a) EV₅ PS₉₅, (b) EV_{7.5}PS_{92.5}, (c) EV₁₀PS₉₀, (d) EV₂₀PS₈₀, (e) EV₃₀PS₇₀, and (f) EV₅₀PS₅₀.

TABLE III
Mechanical Properties of Dynamically Vulcanized 2 wt % Nanoclay-Reinforced EPDM-g-TMEVS/PS Blends

Composition	Izod impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)
EV ₅ PS ₉₅	90.0 ± 7	53 ± 2	2.7 ± 3	86 ± 5	2960 ± 20
EV _{7.5} PS _{92.5}	109.0 ± 2	52 ± 5	3.1 ± 7	84 ± 6	2840 ± 31
EV ₁₀ PS ₉₀	135.0 ± 9	50 ± 4	4.8 ± 3	81 ± 2	2775 ± 27
EV ₁₅ PS ₈₅	115.0 ± 1	47 ± 8	5.6 ± 5	77 ± 8	2490 ± 19
EV ₂₀ PS ₈₀	97.8 ± 4	43 ± 1	6.1 ± 7	70 ± 9	2270 ± 24
EV ₃₀ PS ₇₀	85.0 ± 6	41 ± 4	7.9 ± 2	65 ± 4	2110 ± 32
EV ₅₀ PS ₅₀	78.0 ± 7	40 ± 7	9.0 ± 4	63 ± 3	2000 ± 36
PS ₁₀₀	20.0 ± 3	49 ± 3	2.0 ± 8	82 ± 6	2700 ± 29

PS, wt % of polystyrene; EV, wt % of EPDM-g-TMEVS copolymer.

polystyrene (Table II). It can also be confirmed by SEM micrographs [Fig. 8(a-c)].

Tensile strength and percentage elongation

It is observed that the values of tensile strength of dynamically vulcanized polystyrene blends (Table II) were decreased with the increasing concentration of silane-grafted EPDM on to polystyrene brittle matrix. The introduction of silane-grafted EPDM namely 5, 7.5, 10, 15, 20, 30, and 50% into the polystyrene matrix decreased the values of tensile strength by 8, 14, 18.4, 28.6, 37.8, 40.8, and 46.2%, respectively. However, when compared with linear polystyrene blends (Table I), the values of tensile strength of the dynamically vulcanized polystyrene blends (Table II) were higher than those of linear blends of the same composition. The increase in the values of tensile strength of dynamically vulcanized blends is attributed to the improvement in the crosslinking between the constituent phases of the blends.

The introduction of silane-grafted EPDM into the dynamically vulcanized EPDM-g-TMEVS/PS blends increased the values of (Table II) percentage elongation. The varying percentage incorporation of silane-grafted EPDM namely 5, 7.5, 10, 15, 20, 30, and 50% into the polystyrene matrix increased the values of percentage elongation by 50, 90, 150, 225, 260, 340, and 400%, respectively. The values of percentage elongation of dynamically vulcanized polystyrene blends were lower than those of linear blends because of enhanced intercrosslinking between the blend constituents, which improves the stiffness behavior of the resulting blend [Figs. 3(b) and 4(c)].

Flexural properties

The flexural properties such as flexural strength and flexural modulus of dynamically vulcanized EPDM-g-TMEVS/PS blends were higher than those of linear blends of similar composition. The values of flexural strength of polystyrene blends with increas-

ing percentage incorporation of silane-grafted EPDM namely 5, 7.5, 10, 15, 20, 30, and 50% into the polystyrene matrix were decreased to 6.1, 11, 14.6, 20.6, 26.8, 34.1, and 37.8%, respectively. This can be explained because of flexible silane skeleton, which in turn improved the ductile behavior of polystyrene blends. However, the values of flexural strength and flexural modulus of dynamically vulcanized blends were higher than those of linear blends because of the enhanced crosslinking (graft-link) between rubbery phase and plastic matrix phase imparted by radical initiator [Figs. 5(b) and 6(b)].

Mechanical behavior of nanoclay-reinforced EPDM-g-TMEVS/PS blends

The values of impact strength, tensile strength, percentage elongation at break, flexural strength, and flexural modulus of clay-reinforced blends namely 2 and 4 wt % are presented in Tables III and IV and Figures 2-6.

Impact strength

The impact strength values of EPDM-g-TMEVS/PS blends increased with increasing the percentage concentration of nanoclay. The increase in the values of impact strength may be explained because of better compatibilization between the phases of blend component and smaller size of rubber particles induces the intimate interaction and leads to intercalation, which was clearly observed from XRD analysis (Fig. 11). As the intercalation of rubber-matrix with clay prevents the interfacial separation and thus contributes to the significant improvement in the values of impact strength, it was observed that the values of impact strength of nanoclay-reinforced blends were higher than those of linear- and dynamically vulcanized blends of same composition. For example, the polystyrene blends consisting of 2 wt % nanoclay with silane-grafted EPDM of 5, 7.5, 10, 15, 20, 30, and 50% increased the values of impact

TABLE IV
Mechanical Properties of Dynamically Vulcanized 4 wt % Nanoclay-Reinforced EPDM-g-TMEVS/PS Blends

Composition	Izod impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)
EV ₅ PS ₉₅	98.5 ± 2	56 ± 3	2.4 ± 3	89 ± 3	3040 ± 25
EV _{7.5} PS _{92.5}	118.2 ± 5	54 ± 6	3.0 ± 6	85 ± 5	2950 ± 18
EV ₁₀ PS ₉₀	140.4 ± 1	52 ± 9	4.6 ± 4	83 ± 2	2860 ± 26
EV ₁₅ PS ₈₅	125.0 ± 8	48 ± 4	5.2 ± 8	80 ± 9	2600 ± 32
EV ₂₀ PS ₈₀	101.7 ± 6	46 ± 7	6.0 ± 5	73 ± 6	2440 ± 21
EV ₃₀ PS ₇₀	93.2 ± 3	43 ± 5	7.1 ± 9	68 ± 7	2250 ± 29
EV ₅₀ PS ₅₀	85.0 ± 5	41 ± 1	8.5 ± 3	64 ± 4	2200 ± 30
PS ₁₀₀	20.0 ± 8	49 ± 2	2.0 ± 2	82 ± 3	2700 ± 22

PS, wt % of polystyrene; EV, wt % of EPDM-g-TMEVS copolymer.

strength by 4.5, 5.5, 6.8, 5.8, 4.9, 4.3, and 3.9 times, respectively [Fig. 2(c)]. Similarly, the polystyrene blends with 4 wt % of nanoclay with the silane-grafted EPDM namely 5, 7.5, 10, 15, 20, 30, and 50% increased the values of impact strength by 4.9, 5.9, 7.0, 6.3, 5.0, 4.7, and 4.3 times, respectively. However, the blends with 4 wt % of nanoclay show higher values of impact strength than the blends with 2 wt %, this behavior is due to strong and more intercalation with nanoclay, and thus resulting with improved impact strength [Fig. 2(d)].

Tensile strength and percentage elongation

The values of tensile strength of the nanoclay-reinforced EPDM-g-TMEVS/PS blends were higher than that of unmodified polystyrene (Tables III and IV). Further, the values of tensile strength of nanoclay-reinforced polystyrene blends were also higher than those of linear- and dynamically vulcanized polystyrene blends of similar composition. This trend may be explained because of graft link between the rubbery phase and polystyrene phase and intercalation into clay layers. This may also causes the formation of fine craze structures in the surrounding matrix, which avoids crack propagation and prevents fracture. For example, the polystyrene blends consisting of 2 wt % nanoclay with silane-grafted EPDM of 5, 7.5, and 10% increased the values of impact strength to 8, 6.1, and 2.2%, respectively. Similarly, the polystyrene blends with 4 wt % nanoclay with the silane-grafted EPDM namely 5, 7.5, and 10% increased the values of tensile strength to 14.3, 10.2, and 6.1%, respectively [Figs. 3(c) and 4(b)]. This behavior is due to increasing the *d*-spacing between the clay layers [Fig. 11(c)].

The values of percentage elongation (Tables III and IV) of nanoclay-reinforced EPDM-g-TMEVS/PS blends were lower than those of linear- and dynamically vulcanized polystyrene blends (Tables I and II). For example, the values of percentage elongation of

blends consisting of 2 wt % of nanoclay with EV₅PS₉₅, EV_{7.5}PS_{92.5}, EV₁₀PS₉₀, EV₁₅PS₈₅, EV₂₀PS₈₀, EV₃₀PS₇₀, and EV₅₀PS₅₀ increased by 40, 55, 140, 180, 205, 295, and 350%, respectively. Similarly, the blends with 4 wt % of nanoclay with silane-grafted EPDM namely 5, 7.5, 10, 15, 20, 30, and 50% increased the values of percentage elongation by 20, 50, 130, 160, 200, 255, and 325%, respectively [Figs. 3(d) and 4(a)]. This behavior is mainly because of insertion of blend components into clay layers (intercalation), which imparts rigidity.

Flexural properties

The values of flexural properties (Tables III and IV) of nanoclay-reinforced EPDM-g-TMEVS/PS blends were increased with increasing percentage incorporation of silane-grafted EPDM and with an increasing concentration of nanoclay. This is because of the high stiffness offered by nanoclay upon intercalation, which in turn improved the values of flexural strength and flexural modulus [Figs. 5(c,d) and 6(c,d)].

Hardness of EPDM-g-TMEVS/PS blends

The value of hardness of unmodified polystyrene is 89. When compared with the value of hardness of unmodified polystyrene, the hardness of linear EPDM-g-TMEVS/PS blends decreased from 89 to 79 with increasing the incorporation of percentage composition of silane-grafted EPDM in the polystyrene matrix. It may be explained because of the presence of soft rubbery constituent in the polystyrene matrix, which imparts flexibility to brittle polystyrene and in turn decreased the polymer chain stiffness. The values of hardness of linear blends with 5 and 50 wt % of silane-grafted EPDM are 82 and 79, respectively. The hardness values of dynamically vulcanized EPDM-g-TMEVS/PS blends are higher than that of linear blends because of crosslinking,

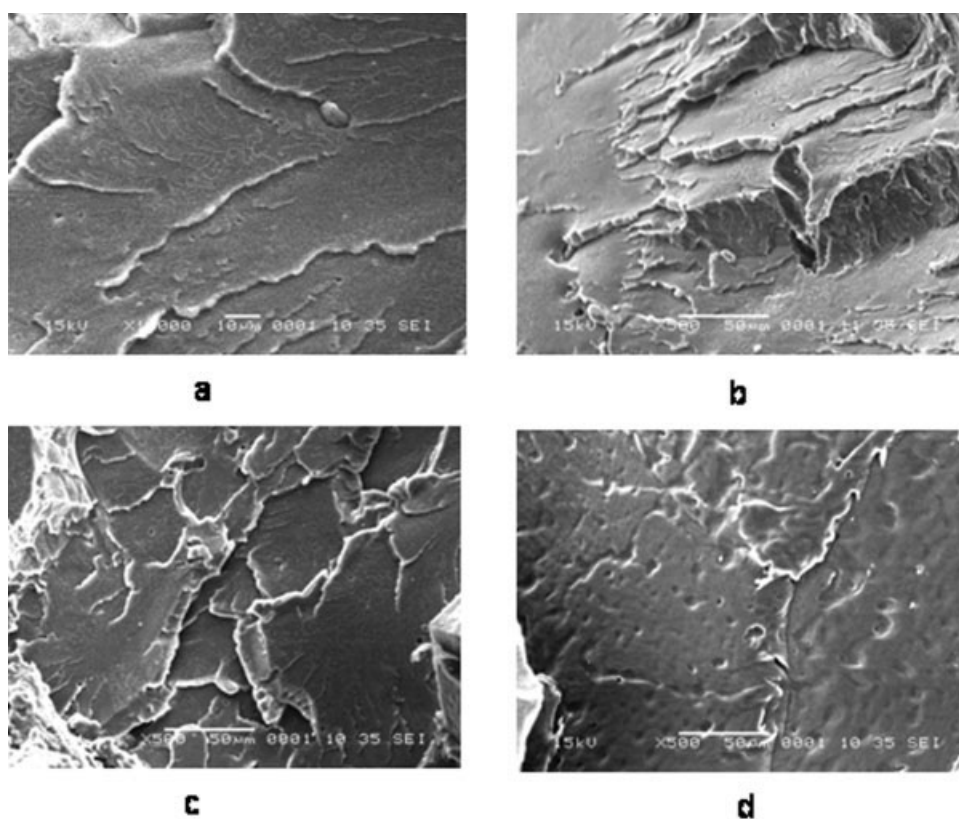


Figure 9 SEM micrographs of 2 wt % nanoclay-reinforced polystyrene blends (a) EV₅PS₉₅, (b) EV_{7.5}PS_{92.5}, (c) EV₁₀PS₉₀, and (d) EV₂₀PS₈₀.

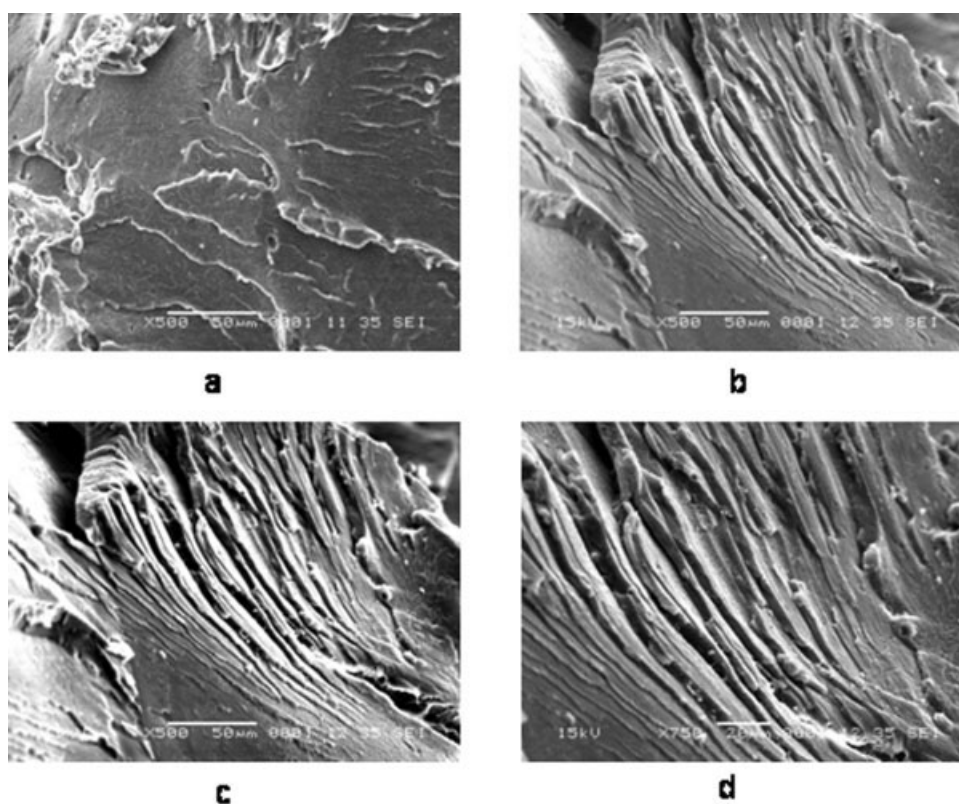


Figure 10 SEM micrographs of 4 wt % nanoclay-reinforced polystyrene blends (a) EV₅PS₉₅, (b) EV_{7.5}PS_{92.5}, (c) EV₁₀PS₉₀, and (d) EV₂₀PS₈₀.

which makes the polymer chain more strong and tough. The values of hardness of dynamically vulcanized blends with 5 and 50 wt % of silane-grafted EPDM are 86 and 81, respectively. The hardness values of nanoclay-filled EPDM-g-TMEVS/PS blends are higher than those of linear- and dynamically vulcanized blends of similar composition. The value of hardness of blends filled with 2 wt % clay is increased from 89 to 92 and that of blends filled with 4 wt % nanoclay is increased from 89 to 95. This trend may be because of the stronger interaction between the nanoclay and blend constituents.

SEM analysis of EPDM-g-TMEVS/PS blends

Scanning electron micrographs of linear blends

The scanning electron micrographs of the fractured surface of the linear EPDM-g-TMEVS/PS blends having varying compositions of rubbery phase are presented in Figure 7. Figure 7(a–c) depicts the micrographs of the blends incorporated with 5, 7.5, and 10 wt % of the silane-grafted EPDM, respectively. The smooth morphology is observed because of that the average particle size of the rubber in the blend is about 1 μm . The small particles influence the compatibility between the dispersed phase and the matrix phase, which in turn enhanced the values of impact strength. Figure 7(d–f) represents the SEM micrographs of the blends consisting of 20, 30, and 50% of silane-grafted EPDM and exhibits the coarse morphology because of the large size of rubber particles and agglomeration and leads to inefficient adhesion between the rubbery phase and plastic matrix phase.

Scanning electron micrographs of dynamically vulcanized blends

The scanning electron micrographs of the fractured surface of the dynamically vulcanized EPDM-g-TMEVS/PS blends with varying weight percentage of rubber are presented in Figure 8. Figure 8(a–c) represents the blends consisting silane-grafted EPDM content of 5, 7.5, and 10 wt %, respectively. They exhibit coarse morphology because of the formation of crosslinks between the blend constituents and also because of enhanced size of rubber particles. Figure 8(d–f) represents micrographs of the blends with 20, 30, and 50% of rubber content, respectively. The phase separated coarse morphology is observed because of the inferior adhesion between the dispersed rubber phase and plastic matrix phase as a result of enhanced size of rubber particles, which in turn lowered the values of impact strength of dynamically vulcanized blends (Table II).

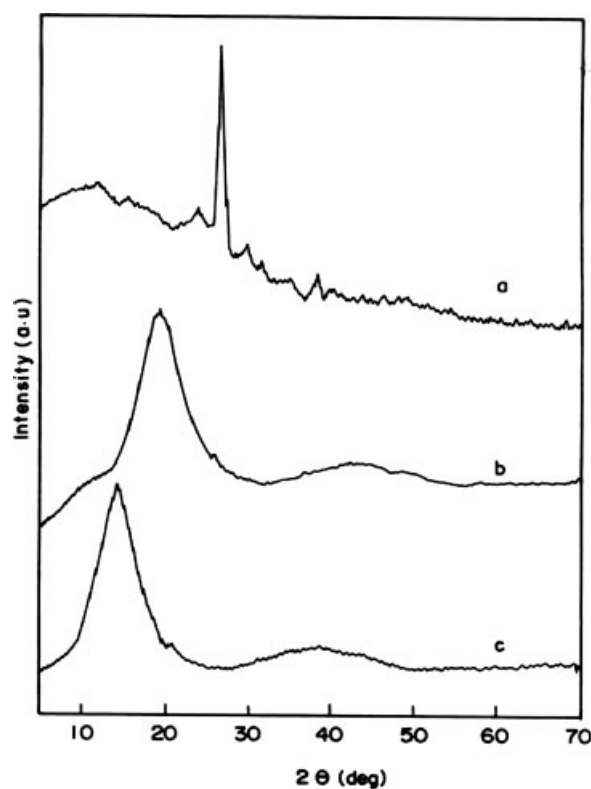


Figure 11 XRD patterns of polystyrene blends (a) organophilic clay, (b) EPDM-g-TMEVS/PS blend with 2 wt % clay, (c) EPDM-g-TMEVS/PS blend with 4 wt % clay.

Scanning electron micrographs of nanoclay-reinforced blends

The scanning electron micrographs of the fractured surface of nanoclay-reinforced EPDM-g-TMEVS/PS blends having varying weight percentages of nanoclay and change in morphology of the EPDM-TMEVS/PS blends as a function of nanoclay content are presented in Figures 9 and 10. Figure 9(a–d) represents the blends EV₅PS₉₅, EV_{7.5}PS_{92.5}, EV₁₀PS₉₀, and EV₂₀PS₈₀ consist of 2 wt % nanoclay incorporation. The SEM micrographs clearly indicated that the clay layers are spread over the whole of the blends, which lead to the formation of the fine and smooth morphology of the blends. Further, it is also observed that the uniform distribution of nanoclay in the blends leads to the retardation of coalescence of dispersed particles. This results in an improved compatibility through intercalation and is responsible for enhancement in the values of impact strength, tensile strength, and flexural properties. Similarly, Figure 10(a–d) represents the blends EV₅PS₉₅, EV_{7.5}PS_{92.5}, EV₁₀PS₉₀, and EV₂₀PS₈₀ with 4 wt % of nanoclay incorporation. The addition of 4 wt % nanoclay into the blends further enhanced the smooth surface of the blends because of strong interaction between the nanoclay and blend constituents.

XRD studies of EPDM-g-TMEVS/PS blends

Figure 11 presents the XRD patterns of (a) organophilic clay, (b) EPDM-g-TMEVS/PS blend filled with 2 wt % clay (EV₁₀ PS₉₀), and (c) EPDM-g-TMEVS/PS blend filled with 4 wt % clay (EV₁₀ PS₉₀). The peak [Fig. 11(a)] observed at $2\theta = 27.03$ corresponds to organophilic clay. The XRD peak [Fig. 11(b)] appeared at $2\theta = 18.92$ corresponding to *d*-spacing of 5.73 nm, indicated the enhancement in gallery height during melt compounding. Further, the disappearance of original nanoclay peak infers the intercalation and the improvement in compatibility because of the reduction in particle size of the blend components. Similarly, the XRD peak [Fig. 11(c)] appeared at $2\theta = 13.51^\circ$ corresponds to *d*-spacing of 6.54 nm, again confirms the reduction of particle size in the blend components involved in the blend system. The XRD results are in good agreement with the SEM analysis.

CONCLUSIONS

A new graft copolymer of TMEVS-grafted-EPDM (EPDM-g-TMEVS) has been developed by grafting of TMEVS onto EPDM using DCP as radical initiator in a twin-screw extruder. The linear blends based on EPDM-g-TMEVS have been developed with varying weight percentages of polystyrene by melt mixing in a twin-screw extruder. The grafting of TMEVS onto EPDM at allylic position present in the third monomer 2-ethyldiene-5-norborene (ENB) has been confirmed by FTIR. From the mechanical studies, it was observed that increasing the values of impact strength with increasing percentage incorporation of silane-grafted EPDM in the linear- and dynamically vulcanized blends are due to the reduction in rubber particle size, which improved the compatibility between the blend constituents. Similarly, the percentage elongation also increases because of increasing molecular chain mobility imparted by silane-grafted EPDM. The values of tensile strength, flexural strength, and flexural modulus of polystyrene blends are decreased with increasing the percentage incorporation of silane-grafted EPDM because of chain flexibility and ductility imparted by silane-grafted EPDM. The blends with 10 wt % of silane-grafted EPDM possess higher values of mechanical properties than those of blends containing beyond 10 wt % of silane-grafted EPDM because of enhanced particle size and consequent phase separation. In the case of nanoclay-reinforced polystyrene blends, the values of impact strength, percentage elongation at break, tensile strength, flexural strength, flexural modulus, and hardness are increased with an increase in the concentration of nanoclay because of efficient interaction between

the clay and blend constituents with interaction of polymer molecules into interlayer clay space. The SEM micrographs of linear blend show fine and smooth surface morphology because of uniform dispersion of EPDM-g-TMEVS phase in the plastic matrix than those of dynamically vulcanized blends. The dynamically vulcanized blends exhibit coarse morphology because of the formation of network structure between the blend constituents. The very fine and uniform surface morphology is observed in the case of clay-reinforced blends because of intimate interaction between the clay and blend constituents. XRD studies indicated that the polymer molecules penetrate into interlayer clay space leading to intercalation. The data resulted from different studies, it is concluded that EPDM-g-TMEVS/PS blends can be used to make automotive components, oil seals, gaskets, and other molded products for interior and exterior applications.

References

- Bucknall, C. B. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2, p 91.
- Wu, S. *Polymer* 1985, 26, 1855.
- Piorkowska, E.; Argon, A. S.; Cohen, R. E. *Polymer* 1993, 34, 4435.
- Ohishi, H.; Ikehara, T.; Nishi, T. *J Appl Polym Sci* 2001, 80, 2347.
- Ramsteiner, F.; Heckmann, W.; Mackee, G. E.; Breulmann, M. *Polymer* 2002, 43, 5995.
- Liu, N. C.; Baker, W. E. *Polym Eng Sci* 2004, 32, 1695.
- Bucknall, C. B. In *Rubber Modified Polymers*; Allen, G.; Bevington, J. C.; Eastmon, G. C.; Ledwith, A.; Russo, S.; Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; Vol. 10, p 27.
- Wu, J.; Guo, B.; Chan, C. H.; Liand, J.; Tang, H. S. *Polymer* 2001, 42, 8857.
- Dompas, D.; Groenincky, G. *Polymer* 1994, 35, 4743.
- Zhang, Q.; Yang, H.; Fu, Q. *Polymer* 2004, 45, 1913.
- Feng, W.; Isayeu, A. I. *Polymer* 2004, 45, 1207.
- Utracki, L. A. *Polymer Alloys and Blends*; Carl Hanser: New York, 1990.
- Eklind, H.; Maurer, F. H. J.; Steeman, P. A. M. *Polymer* 1997, 38, 1047.
- Cartier, H.; Hu, G. *Polymer* 2001, 42, 8807.
- Lourenco, E.; Felisberti, M. I. *Eur Polym J* 2006, 42, 2632.
- Crevecoeur, J. J.; Mencer, J. H.; Hogt, M. A. *Polymer* 1995, 36, 753.
- Pticek, A.; Hrnjak-Murgic, Z.; Jeelencia, J. *Exp Polym Lett* 2007, 3, 173.
- Shaw, S.; Singh, R. P. *J Appl Polym Sci* 1990, 40, 685.
- Shaw, S.; Singh, R. P. *J Appl Polym Sci* 1990, 40, 693.
- Shaw, S.; Singh, R. P. *J Appl Polym Sci* 1990, 40, 701.
- Ramar, P.; Alagar, M. *Polym Adv Tech* 2004, 15, 377.
- Chitrangad, B.; Middleman, S. *Macromolecules* 1981, 14, 352.
- Wang, W.; Qu, B. *Polym Degrad Stab* 2003, 81, 531.
- Schultz, D. L. *Rubber World* 1981, 184, 36.
- Alexander, M.; Dubois, P. *Mat Sci Eng* 2000, 28, 1.
- Chen, D.; Yang, H.; He, P.; Zhang, W. *Comp Sci Technol* 2005, 65, 1593.

27. Hussain, F.; Hojjati, M.; Okamoto, M.; Gorga, R. E. *J Comp Mater* 2006, 40, 1511.
28. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
29. Usuki, A.; Hasegawa, N.; Kato, M.; Kobayashi, S. *Adv Polym Sci* 2005, 179, 135.
30. Maniar, A. A. *Polym Plast Tech Eng* 2004, 43, 427.
31. Pinnavaia, T. J.; Brall, G. W., Eds. *Polymer Clay Nanocomposites*; Wiley: New York, 2000.
32. Yu, Z.-Z.; Yan, C.; Yang, M.; Mai, Y.-W. *Polym Int* 2004, 53, 1093.
33. Kausch, H. H.; Michler, G. H. *J Appl Polym Sci* 2007, 105, 2577.
34. Choi, H. J.; Kim, T. H.; Lim, S. T.; Lee, C. H.; Jhon, M. S. *J Appl Polym Sci* 2003, 87, 2106.
35. Usuki, A.; Tukigase, A.; Kato, M. *Polymer* 2002, 43, 2105.
36. Wills, J. M.; Favis, B. D.; Lunt, J. *Polym Eng Sci* 2004, 30, 1073.
37. Mishra, J. K.; Chang, Y.-W.; Choi, N. S. *Polym Eng Sci* 2007, 47, 863.
38. Dinakaran, K.; Alagar, M. *Polym Adv Tech* 2003, 14, 574.
39. Kornmann, X.; Lindberg, H.; Berglard, L. A. *Polymer* 2001, 42, 1303.