Comparison of Ethylene-Propylene Diene Terpolymer Composites Filled with Natural and Synthesized Micas

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ABSTRACT: In this paper, EPDM/mica composites were prepared by filling synthesized mica and natural mica separately into ethylene-propylene diene terpolymer (EPDM) using melt blending technique. Microstructures, electrical properties, gas resistance, and mechanical properties of two EPDM/mica composites were investigated systematically. FTIR show that hydroxyl groups exist on the surface of the micas. These structural hydroxyls could be active sites conducive to the surface modification of mica. XRD analyses reveal that the natural mica is crystalline and the synthesized mica is amorphous. After being modified with silane coupling agent Si69, mica was only exfoliated into smaller micron agglomerates dispersing in EPDM, but the dispersion of amorphous synthesized mica was better. So the EPDM/synthesized mica composite possessed better mechanical property, electrical insulation property, and gas permeability resistance. It is expected that better improvement would be achieved, if mica is exfoliated further into nanosheets dispersing in the rubber matrix. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3184–3192, 2010

Key words: ethylene-propylene diene terpolymer; mica; composites; properties

INTRODUCTION

Many researchers have always been attracted to study the reinforcement of rubber.[1–4] Generally, rubber products were filled with about 50% of filler to improve the performances, especially mechanical properties and processing properties, as well as to reduce the cost. According to the shape of fillers, they can be divided into layered structured materials (such as montmorillonite and mica), fibrous reinforcements (polyester fiber and carbon nanotubes), and particulate fillers (such as carbon black and silica). In the last decades, besides the traditional carbon black and silica, a lot of newly developed fillers, such as montmorillonite, nano-magnesium hydroxide, and carbon nanotubes, have been attempted to be used in rubber. It has been found that those novel fillers not only improve the mechanical properties of rubber significantly but also impart unique properties such as excellent gas barrier properties (MMT), flame retardancy (nano-magnesium hydroxide), and electrical conductivity (carbon nanotubes) to rubber.[5–7] Wu et al. prepared a variety of rubber matrix/clay nanocomposites by blending montmorillonite in aqueous solution with the rubber latex.[8,9] The clay nano-layers dispersed in rubber matrix showed remarkable reinforcement and significantly improved gas barrier properties of rubber, which made it potential to be applied in tire inner liner.[5]

Mica is another type of layered structured silicate. It has been widely used as reinforcing filler in polymeric matrices because of its excellent electrical insulation, thermal stability, water resistance, chemical resistance, flexibility, and high-spin-off properties.[10] Mica is used to strengthen plastics, and composites such as polyether ketone/mica, polylactic acid/mica, polyolefin/mica, polyester/mica, polyamide/mica, polyurethane/mica are well-known. It was accepted that mica could enhance the strength modulus and thermal resistance of plastic and reduce warpage phenomenon as well.[10–15] Daniele et al.[16] studied the natural rubber (NR) and polybutadiene vulcanizates(BR) filled with the mineral mica, respectively, and found that tensile strength of NR vulcanizates was increased from 15 to nearly 19 MPa as the amount of mica was increased from 0 to 30 phr, showing a peak value at the loading amount of 20 phr. However, mica-BR composites changed little in tensile strength. Furtado et al.[17] found that 300% tensile stress of styrene butadiene

TABLE I
Formulation for Rubber Compounding

Component	Phr
EPDM4045	100
ZnO	5.0
SA	1.0
Si69	6.0
Accelerator M	0.5
Accelerator TT	1.0
Accelerator CZ	1.0
Sulfur	0.8
Mica	Variable

M, TT, and CZ are trade names.
M, 2-mercaptobenzothiazole; TT, tetramethylthiuram disulfide; CZ, N-cyclohexyl-2-benzothiazyl sulfonamide.

rubber/silica composites could be markedly enhanced by adding mineral mica modified with silane coupling agent (Si69), while the tensile strength and tear strength didnot show significant improvement.

Ethylene-propylene diene terpolymer (EPDM) has excellent electrical insulation, weather-resistance, water-resistance, and wide service temperature (-50 to $125°C$). It is extensively used to prepare flexible material with excellent electrical insulation properties, which is widely applied to wire/cable insulation coverings and insulation layers. In addition, with excellent ozone-resistant properties and processing properties, EPDM is also often blended with butyl rubber (IIR) to improve the processing and ozone-resistant properties of IIR for preparing tire inner tube, but the gas resistance of IIR is reduced. Based on the excellent performance of mica and EPDM, EPDM/mica composites were prepared by filling synthesized mica and natural mica separately into EPDM terpolymer using melt blending technique in this work. This report focuses on the chemical structure of the two types of micas. And the effect of the two types of micas on the mechanical property, electrical insulation property, and gas permeability resistance of EPDM/mica composites was studied in detail.

EXPERIMENT

Material

Ethylene-propylene diene terpolymer (EPDM4045) was purchased from Petroleum Organic Synthesis Factory, Jilin province, China. Synthesized mica powder was supplied by Sinoma Advanced Materials, Shandong province, China; natural mica was bought from Jiangxi Copper Company, Jiangxi province, China. Bis(3-triethoxysilylpropyl)tetrasulfide

$(Si69(C_2H_5O)_3Si(CH_2)_3S_4Si(CH_2)_3(OC_2H_5)_3)$ was supplied by Nanjing Shuguang Chemical Company, China. Other chemicals including rubber curing additives ZnO, stearic acid (SA), accelerators, and sulfur were bought from stores and used as received.
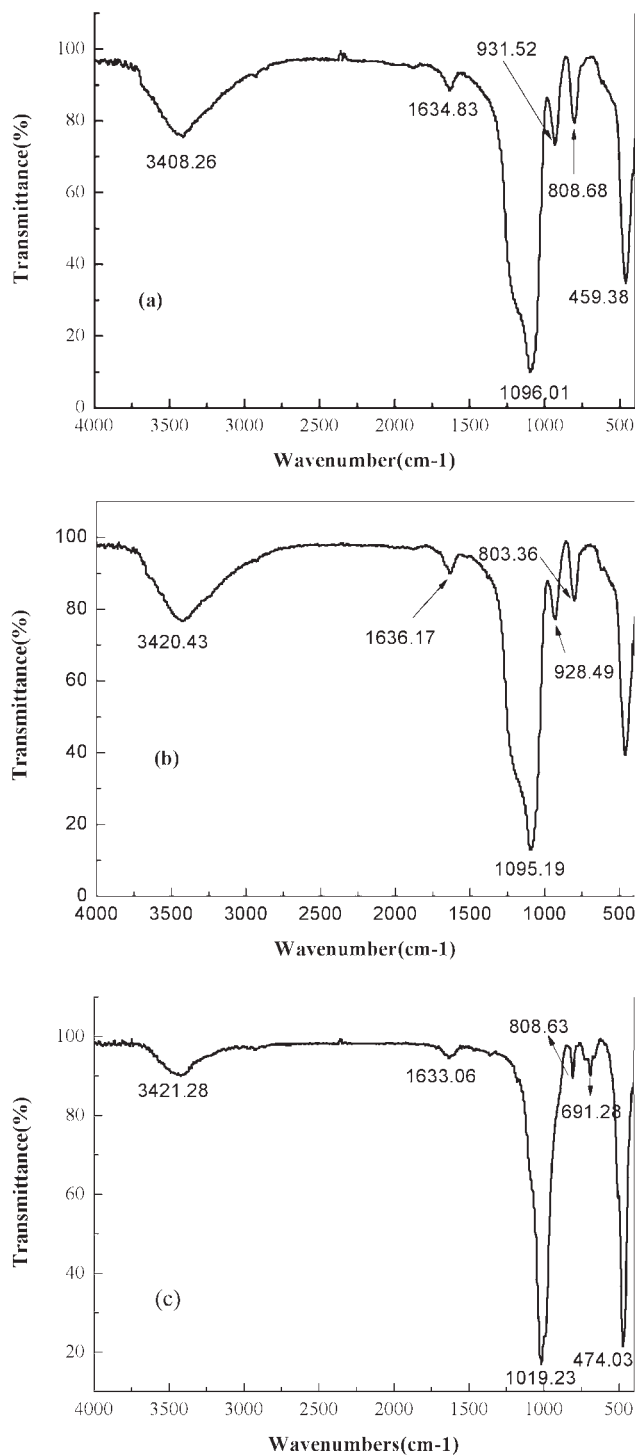

Figure 1 IR spectra of mica: (a) synthesized mica undried, (b) synthesized mica dried at $120°C$ for 2 h, and (c) natural mica dried at $120°C$ for 2 h.

TABLE II
Classification of Absorption Bands in Figure 1

Wave length (cm^{-1})	Classification
474.03/459.38	Bending vibration of Si—Mg
691.28	Bending vibration of Si—O—plane
808.63/808.68	Bending vibration of OH in Al—OH—Mg
931.52/928.49	Bending vibration of OH in Al—OH— Al
1019.23/1095.19	Stretching vibration of Si—O
1633.06/1634.83	Bending vibration of the adsorbed water
3408.26	Stretching vibration of OH in free water
3421.28/3420.43	Stretching vibration of OH in hydrogen bonds formed by oxygen on Al—OH—Si surface and the water between layers

Figure 2 X-ray diffraction patterns of two types of micas.

Preparation of composites

The compositions of rubber compounding used for this study are shown in Table I. Mica was used as the filler in the range varying from 0 to 40 phr (mass fraction).

Mica modification

To improve filler-rubber interface adhesion, surface treatment of mica is necessary. A 10–20% aqueous suspension of mica was put into high-speed agitator and agitated at the speed of 800 r/min to make mica exfoliated into nanosheets. Then, the mixture of Si69/alcohol at the mass ratio of about 1 : 5 was added slowly and uniformly to the above
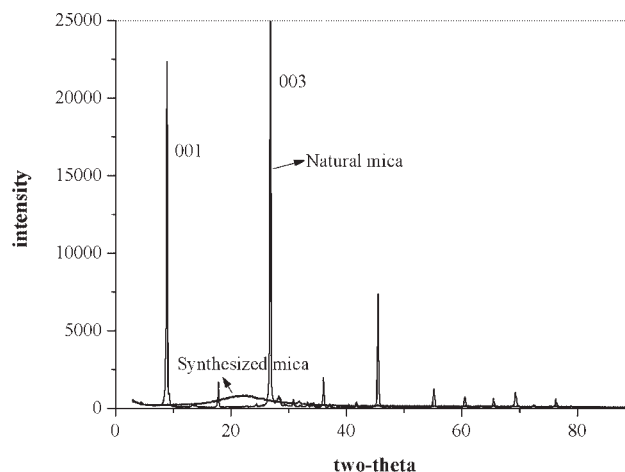
suspension, which was treated for 30 min at 60°C. The solvent was then removed to get dry solid particles, which were ground to powders. Si69 amount was 6% mass fraction of mica.

Composite preparation

According to the compositions shown in Table I, ZnO, SA, accelerators, mica, and sulfur were added to EPDM step by step on the two-roll mill (φ160 × 320, made in Zhanjiang machinery factory, Guangdong province, China) to achieve a good dispersion
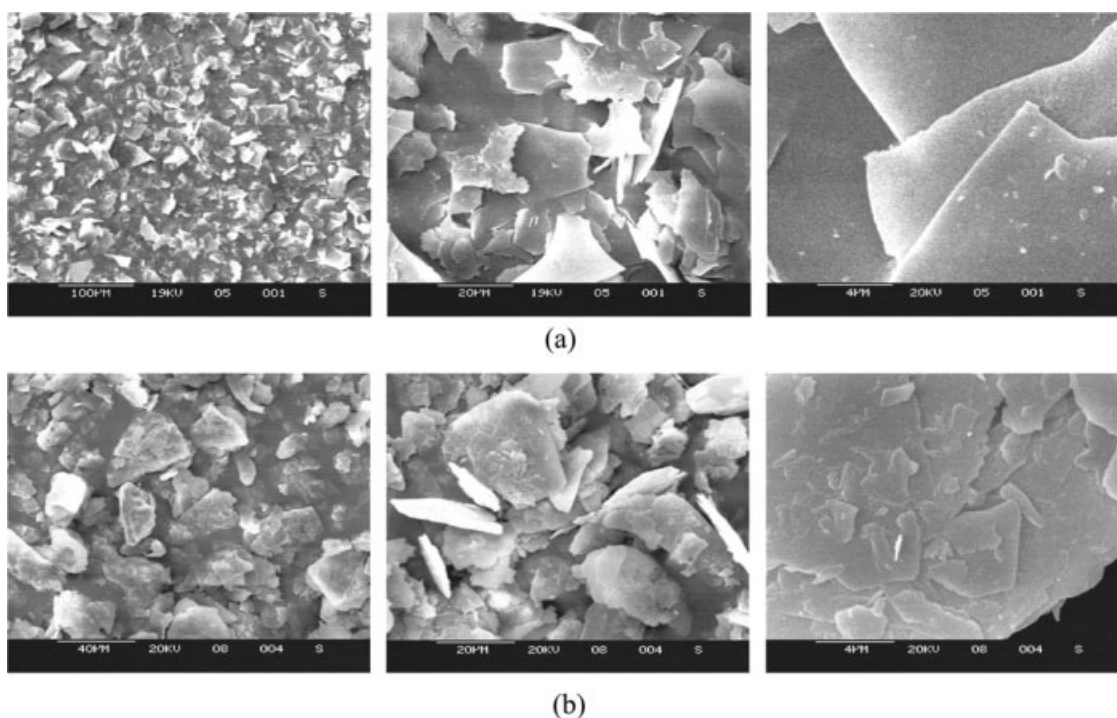

Figure 3 SEM micrographs of two types of micas: (a) synthesized mica, and (b) natural mica.

TABLE III
The Particle Size Distribution of Mica(in Width Direction)

Distribution parameter	Synthesized mica (µm)	Natural mica (µm)
D10	6.06	5.25
D25	9.96	9.66
D50	15.58	16.36
D75	22.21	25.09
D90	28.59	34.07

of the ingredients of the compound. Cure time was determined by disc oscillating rheometer (P3555B2, produced by Central Peak Chemical Machinery Company of Beijing, China) at 160°C. The compound was vulcanized at platen press with 25 ton pressure. Test specimens are cut from vulcanized material according to the gauged die.

Characterization and tests

Tensile test of the composites are carried out according to ASTM D412. During tensile test, five specimens are needed to give the average value.

For the FTIR studies, 1–2 mg finely ground mica samples were mixed with 100–200 mg dry KBr powder and ground for 2–5 min and load into the mould. Circular samples with 13 mm diameter were made by applying 10 ton pressure for 5 min. An FTIR spectroscope, Nicolet 210, was used to study the samples at a scanning frequency of 32 per min. The resolving power was 4 cm^{-1}, and wave number range was 4000–400 cm^{-1}.

A Cambridge (British) S-250MK3 scanning electron microscope (SEM) was used to observe the cryo-fractured surface morphology of the composites. And a Hitachi H-800 transmission electronic microscope (TEM) was used to observe the dispersion of mica in the composites microtomed at −100°C.

After mica was uniformly dispersed in water, its particle size and size distribution were determined by using laser particle size analyzers made by OMEC Technology.

X-ray diffraction patterns of micas and the composites were carried out using a Rigaku X-ray diffractometer (Japan) with CuK$_\alpha$ radiation. The scanning rate was 6.00°/min over a range of 2θ = 3–85°.

Volume resistivity test

The sample surface was cleaned by alcohol and covered with copper foil with conductive adhesive at both sides. The double-cantilever electric bridge (Model QJ36) and high-resistance instrument were used to test resistance value. Volume resistivity (ρ_V) of the sample is calculated as: $\rho_V = RS/h$, where R, S, and h stand for the specimen resistance, surface area and thickness, respectively.

Gas permeability test

The home-made gas permeability tester is mainly composed of specimen cavity, gas channel, gas analysis equipment, and thermostat bath, where the gas analysis equipment is the gas chromatography analyzer. Ventilation rate of nitrogen was tested at constant pressure. The diameter of circular specimen was 8 cm, and the thickness testing was repeated five times to give the average value at 40°C.

RESULTS AND DISCUSSION

The structure of mica

The IR spectra of the two types of micas are shown in Figure 1, and various absorption peaks are listed
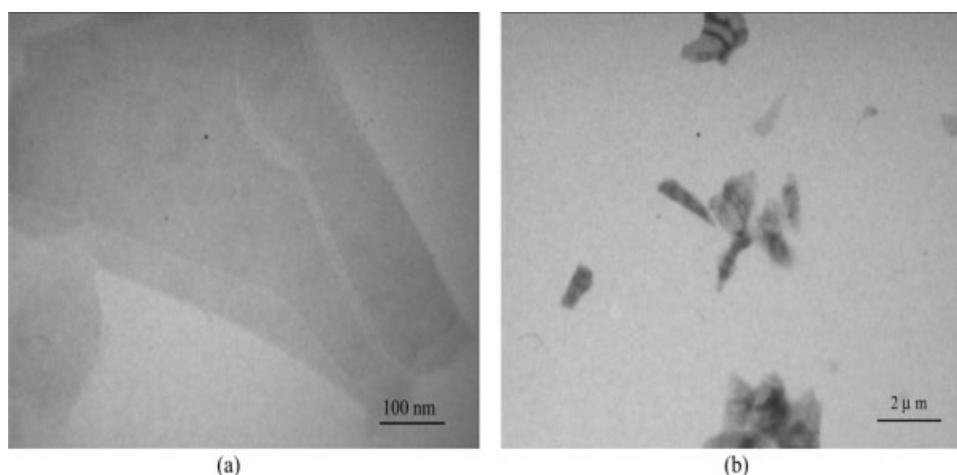

(a)   (b)

Figure 4 TEM photos of mica dispersed in water: (a) synthesized mica, and (b) natural mica.
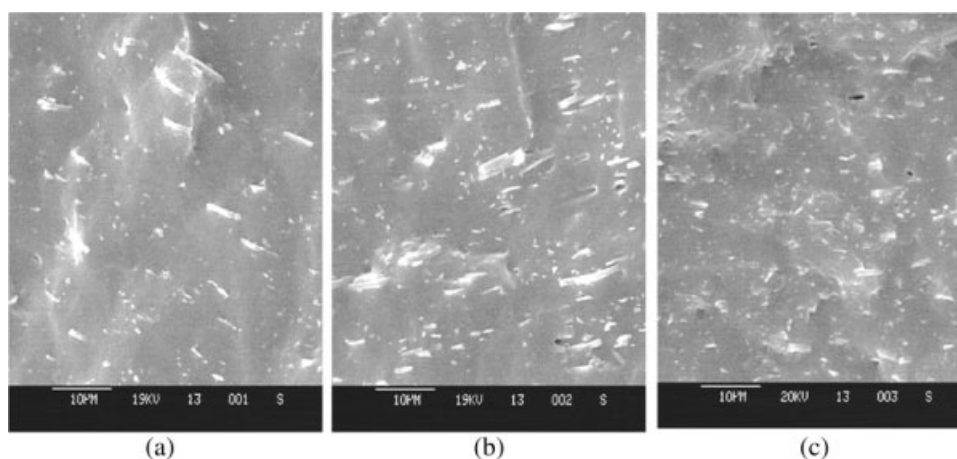
Figure 5 SEM micrographs of cut surface perpendicular to the horizontal plane of EPDM/ synthesized mica composites at varying concentrations of mica: (a) 10 phr, (b) 20 phr, and (c) 40 phr.

in Table II. It can be seen that the IR spectra of the two-mica are very similar and both of them belong to a kind of magnesium silicate (aluminum). A strong absorption peak at 3408 cm^{-1} of the undried synthesized mica indicates the stretching vibration of the hydroxyls (OH) in free water. After the synthesized mica and natural mica were dried at 120°C for 2 h, there appeared OH stretching vibration at 3424.43/3421.28 cm^{-1}, respectively, which is formed by the oxygen of Al—H—Si surface and the hydrogen of the bonded water between mica layers. These structural OH could be active sites conducive to the surface modification of mica. It was reported that the fillers with OH, such as silica and fibrillar silicate, the modifier used in surface modification was related with the vulcanizing system of rubber.[18] In this study, the sulfur was used as the crosslinking agent of EPDM, so Si69 was prefered to modify mica. For synthesized mica, the visible peaks at 808.68/803.36 cm^{-1} and 931.52/928.49 cm^{-1} imply the bending vibration of OH in Al—OH—Mg and Al—OH—Al individually. The aluminum of Al—OH—Al in natural mica is substituted by Mg, so we did not observe the bending vibration absorption peak of OH in Al—OH—Al at 931.52/928.49 cm^{-1}. It could be concluded that the chemical compositions of two types of micas are a little different.

Figure 2 shows X-ray diffraction patterns of the two types of micas. The XRD diffraction peak of synthesized mica is very wide and weak, implying a type of amorphous mica. It was observed that two very strong and narrow diffraction peaks at $2\theta = 8.9°$ and $26.8°$ were attributed to 001 and 003 planes of natural mica. This suggests that natural mica is a clay mineral with relatively complete crystallization.

Figure 3 presents the SEM micrographs of the two types of micas. It can be seen that synthesized mica is a kind of micro-sized agglomerates with the width
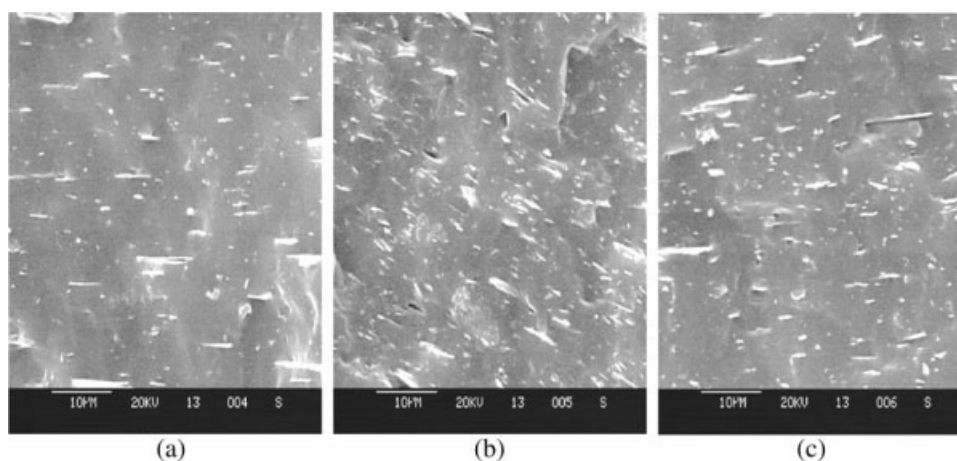

Figure 6 SEM micrographs of cut surface perpendicular to the horizontal plane of EPDM/natural mica composites at varying concentrations of mica: (a) 10 phr, (b) 20 phr, and (c) 40 phr.
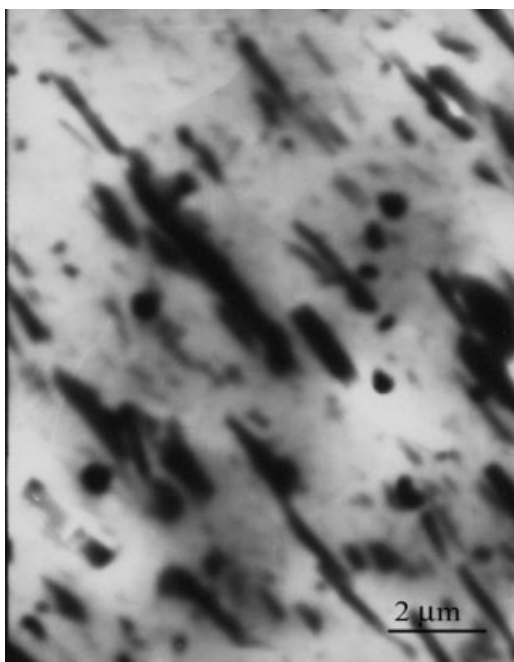
Figure 7 TEM micrographs of the sections cut parallel to the horizontal plane of EPDM/synthesized mica composites (40 phr).

of 10–20 μm and thickness less than 1 μm (the aspect ratio is about 10–20), which is formed by stacking of several inerratic coarse lamellas with smooth surface. Natural mica seems to have the similar structure as synthesized one. But the surface of natural mica is relatively rough, with clear attachments, possibly of impurities. Table III shows the particle size distribution of the two types of micas (in width direction). They have the close particle size as well as the size distribution. Synthesized mica has particle sizes from 6.06 to 28.59 micron. More than 90% agglomerates of synthesized mica are about 28 micron. Natural mica is slightly larger than synthesized one of which most of agglomerates are about 35 microns. This agreed to the result of SEM observation. Both of the micas were dispersed in water with ultrasonically induced agitating as shown in Figure 4. Synthesized mica was well dispersed in water as inerratic thin sheets with the thickness of only a few nanometers, whereas natural mica was dissociated into the smallest irregular crystal units.

The microstructure of the composites

After being modified with Si69, the two types of micas were filled into EPDM rubber by mechanical blending to get EPDM/mica composites. Figures 5 and 6 reveal SEM micrographs of fracture surface of the EPDM/mica composites that were cut

perpendicularly to the horizontal plane of mica. Both micas were found to disperse in rubber matrix as different micron sizes of agglomerates (white strips on the fracture surface), but these dispersed agglomerates became smaller in both width (the length of white strips) and thickness (the width of white strips) compared with original ones. As discussed previously, mica is composed of lots of stacked lamellas. By mechanical shearing during blending process, they were exfoliated into very smaller agglomerates dispersed in rubber matrix, and most of dispersing units were orientated along the shear direction. It can also be observed from Figure 7 that the majority of scattered lamellas of mica aligned along the shear direction. Because mica has a strong interlayer force similar to montmorillonite, it is difficult for mica to be exfoliated into mono-dispersed sheets by direct mechanical blending with rubber matrix, as observed in Figure 4. By increasing the filler content, the number and sizes of mica agglomerates on the fracture surface also increased, implying that the dispersing of mica became poor. Although mica was modified with Si69, those nanosheets still restacked firmly after the removal of water because of the strong interlayer forces.

As seen from Figures 5 and 6, it is evident that synthesized mica dispersed in EPDM better than natural mica. As the dispersing units exfoliated, the particle appeared in smaller width and thickness. There were a few holes on the fracture surface resulted from the pullout of mica from rubber matrix, indicating poor interfacial interactions between rubber and mica. At same loading of mica, EPDM/synthesized-mica composite exhibited stronger interfacial adhesion than EPDM/natural mica composite, especially at higher mica concentrations. As reported
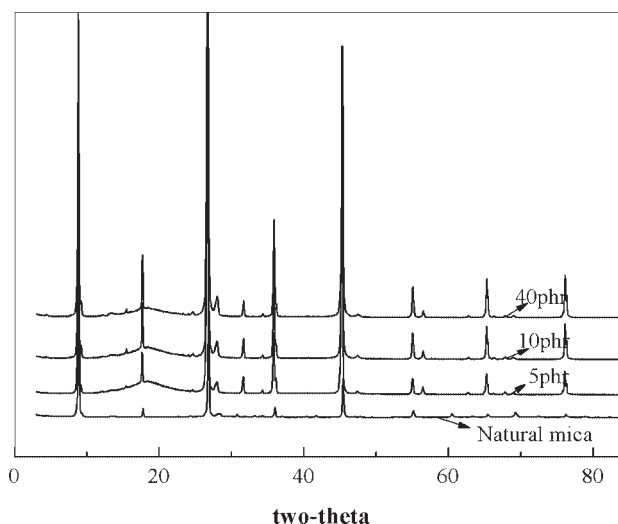

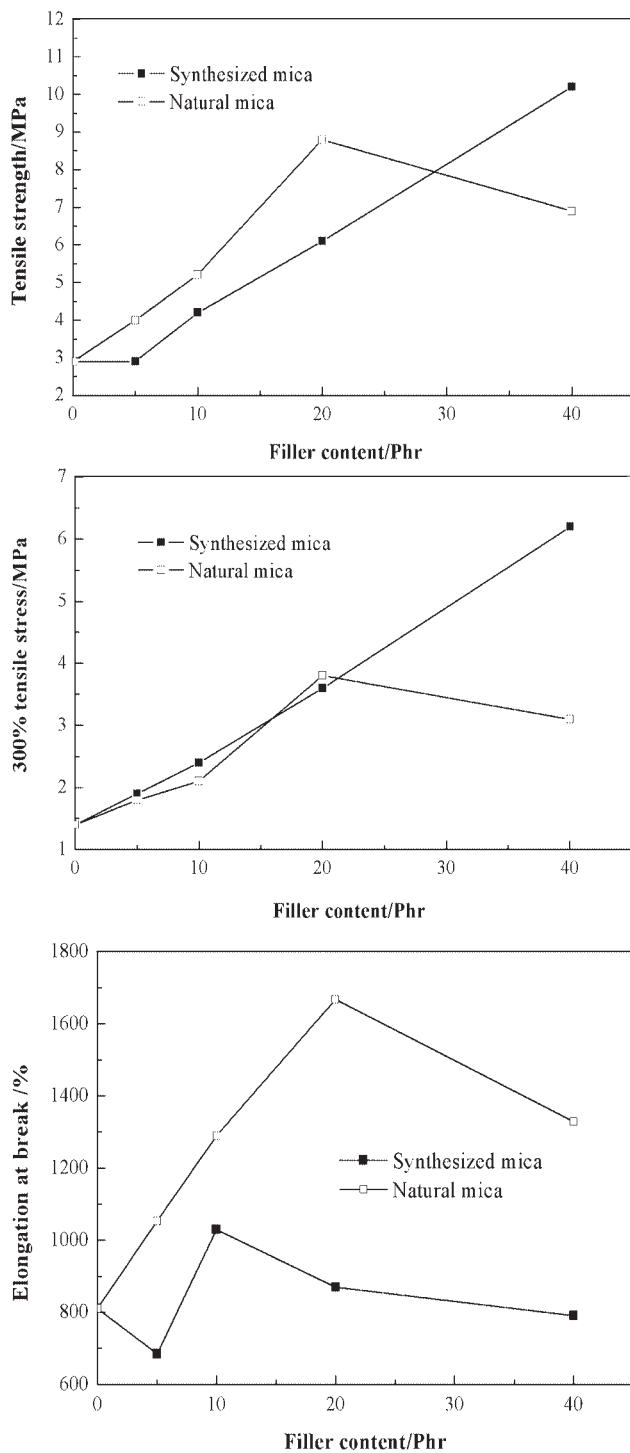**Figure 8** X-ray diffraction patterns of EPDM/natural mica composites.

Figure 9 Dependence of 300% tensile stress, tensile strength, and elongation at break of the composites on filler content.

Compared with X-ray diffraction pattern of natural mica earlier, there was little change in EPDM/natural mica composites in Figure 8. This demonstrated that natural mica still kept the full crystalline structure and no rubber molecular chains inserted into the nanosheets of mica to increase the distance between them. These behaviors were supported by SEM observations. Because synthesized mica is amorphous, it is unavailable to identify the EPDM/synthesized-mica composite by XRD.

The properties of the composites

Mechanical properties

Seen from Figure 9, both EPDM/mica composites show much higher 300% tensile stress and tensile strength than unfilled EPDM. The 300% tensile stress and tensile strength of unfilled EPDM were only 1.4 MPa and 3.0 MPa, respectively. In the case of EPDM/synthesized mica composite, by increasing the filler content the 300% tensile stress and tensile strength also increased until the tensile strength reached up to 10.2 MPa at 40 phr. As to EPDM/natural mica composite, both 300% tensile stress and tensile strength reached the maximum at the loading amount of 20 phr, and then decreased with further addition of mica. EPDM/natural mica composite showed more than 1000% elongation at break, much higher than unfilled EPDM (811%), whereas EPDM/synthesized mica composite possessed elongation at break close to unfilled EPDM. Despite both micas not reaching the exfoliation to nanosheets as we expected, they showed a positive reinforcement to EPDM. As known, mica has a large aspect ratio (10 : 20) as well as very high elastic modulus, so it could bear the load transferred from the matrix through rubber-filler interface according to the mechanism of

by Hendrik,[19] the interaction between hydrophilic mica and majority of hydrophobic rubber is generally poor. It was certain that surface modification of mica improved the interfacial bonding. However, the interfacial contact area was limited because of the poor dispersion of mica.
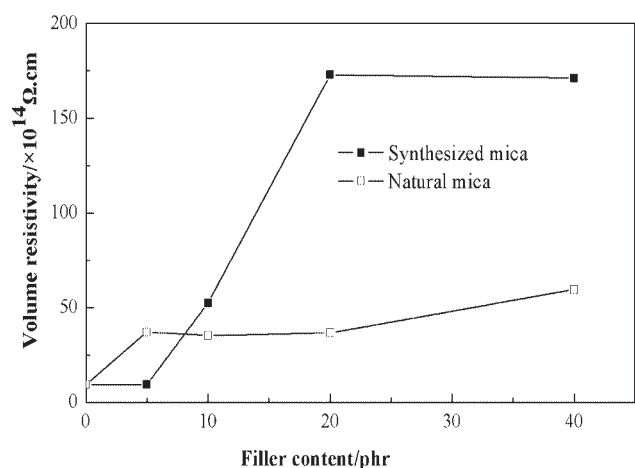
Figure 10 Dependence of volume resistivity of the composites on filler content.

TABLE IV
Permeability Coefficient of EPDM/ Mica Composites

Type of filler	None	Synthesized mica		Natural mica	
The loading amount of filler (phr)	0	10	40	10	40
N_2 Permeability coefficient ($\times 10^{-18}$ Pa^{-1} m^2 s^{-1})	107	87.9	51.2	84.7	68.7

short fiber reinforced rubber composites.[20] Under tensile force, it is easier for nanosheets of mica to glide past each other rather than the occurrence of exfoliation, so that this will positively contribute to elongation; however, the tensile stress may not be increased. As a result, the EPDM composites presented higher elongation at break than unfilled EPDM. This obviously differs from carbon black/silica reinforced rubber composites of which elongation at break reduces with the increase of filler amount.[21] At higher content of mica, the poorer dispersion of mica might cause stress concentration sites, which could initiate to fracture, resulting in the composites which only bear a lower load leading to the lower tensile strength. Even so, it is believed that the reinforcement would be further improved if better dispersion of mica could be achieved.

Electrical property

It is well known that mica possesses excellent electrical insulation property, such as high insulation strength, dielectric constant stability, low power loss, and high resistivity.[22] As seen from Figure 10, EPDM/mica composites exhibited higher volume resistivity than unfilled EPDM, proving that adding mica can improve electrical insulation property of EPDM. Containing 20 phr of mica, volume resistivity of EPDM/synthesized mica composite increases nearly twenty times, whereas the composite filled with natural mica reaches six times. In the case of EPDM/synthesized mica composite, the volume resistivity rises rapidly until the loading level of 20 phr and hereafter the value remains unaltered. It can be explained that with the filler content increased, the dispersing of mica in rubber matrix became poor. The volume resistivity of EPDM/natural mica composite changes little as the amount of mica increases. This testifies that amorphous synthesized mica improves electrical insulation better more than the crystalline natural mica. It is possible that some impurities that the latter includes and its poor

dispersion both may affect its electric insulation property.

Gas permeability

It can be seen from Table IV that the permeability coefficients of EPDM/mica composites are significantly lower than that of unfilled EPDM. As mica concentration increases further, the permeability coefficient decreases. At the loading amount of 40 phr, the permeability coefficient of EPDM/synthesized mica composite reduces nearly 50%, the decrease is by 40% in the EPDM/natural mica system. This implies that the addition of mica could improve the gas permeation resistance of EPDM. Similar to montmorillonite, mica with layered structures can block the gas pass through and extend the gas diffusion path. Therefore, the permeability coefficients of the composites are reduced.

CONCLUSION

Synthesized mica is amorphous, and natural mica is crystalline. Both micas are micron agglomerates composed of the firmly stacked nanosheets. Hydroxyls were proved to exist in the micas. Both types of micas modified with Si69 were exfoliated into smaller micron agglomerates dispersing in EPDM by mechanical blending. Synthesized mica exhibited better reinforcement than the other because of better filler dispersion as well as rubber-filler interfacial adhesion. Also, EPDM/synthesized mica composite possessed better electrical insulation property and gas permeability resistance. It is expected that more improvement would be achieved, if mica was exfoliated further into nanosheets dispersing in the rubber matrix.

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