# Preparation and Properties of New EPDM/Vermiculite Nanocomposites

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Novel nanocomposites based on ethylene-propylenediene rubber (EPDM) and maleic anhydride-modified vermiculite (VMT) were prepared. Maleic anhydride (MA) acts both as the intercalation agent for VMT and as a vulcanizing agent for EPDM matrix. It also acts as a compatibilizer for EPDM and VMT phases. From analysis by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), the silicate layers of the VMT were exfoliated and dispersed uniformly in the EPDM matrix as monolayers. The thermal properties of the nanocomposites were investigated by dynamic mechanical thermal analysis and thermogravimetric analysis; a strong rubber-filler interaction in the nanocomposites was manifested in the measured temperature range by the result of storage modulus. At the same time, there was some enhancement in degradation behavior between the nanocomposites and EPDM matrix. The nanocomposites exhibited a great improvement in tensile strength and modulus, as well as elongation at break. Finally, the effects of MA addition on the formation of nanometric reinforcement and on the mechanical properties of nanocomposites are discussed. POLYM. COMPOS., 26: 706-712, 2005. © 2005 Society of Plastics Engineers

## INTRODUCTION

Polymer/clay nanocomposites have been extensively studied in recent years because they exhibit physicochemical properties dramatically different from those of pure polymers and their microcomposite counterparts [1–5]. They are particle-filled polymers in which at least one dimension of the dispersed particles is in the nanometer range of <100 nm. Because of the small size of the structural unit and the high surface-to-volume ratio, the properties of nanocomposites are greatly influenced by the nanometer-size dispersed particles. For example, they possess improved mechanical properties, thermal stability, flammability resistance, electrical insulation, and barrier properties in comparison with the pure polymer or conventional composites. The structure and properties of nanocomposites depend either on the extent to which the organic and inorganic components are made compatible or on the degree of mixing between the two phases [6-9].

Because ethylene-propylene-diene rubber (EPDM) is a widely used rubber, EPDM-clay composites should have great commercial potential. However, EPDM does not include any polar groups in its backbone; therefore, the homogeneous dispersion of a clay layer in the EPDM matrix would be difficult to realize. Therefore, various clays are pretreated with organometallic ions to increase their surface organophilicity to improve the compatibility between the clays and polymer matrices. Recently, Young et al. [10] reported the intercalated structure of EPDM/OMMT nanocomposites containing octadecylammonium ions and EPDM, in which the presence of fairly large stacks of clay layers indicated a poor dispersion of clay. Another problem with rubber is that long molecular chains are rather difficult to diffuse into the galleries of silicate because of the polarity difference between apolar polymers and polar silicates. More recently, Tjong et al. [11] introduced maleic anhydride (MA) functional groups into vermiculite (VMT) galleries to produce MA-intercalated VMT (MAV). EPDM can be blended with MAV to form a ternary molecular structure (VMT-MA-EPDM) in the presence of benzoyl peroxide (BPO). In such a structure, MA serves as a modifying additive for the EPDM matrix and as a swelling agent for VMT. Then the long molecular chains of the EPDM are easy to diffuse into the galleries of VMT and the homogeneous dispersion of VMT layer in the EPDM matrix is successfully realized.

However, there is no literature about the preparation of EPDM/VMT nanocomposites, especially for MA-treated VMT. VMT is one kind of silicate that is abundant and much cheaper than montmorillonite, hetorite, and saponite. It is generally used as a packaging material for antishocking.

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This work is the first report on the fabrication of the lowcost EPDM/VMT nanocomposites using MA as a reactive reagent that acts both as a modifying additive for the EPDM matrix and as a swelling agent for the VMT. At the same time, MA also acts as a vulcanizing agent for EPDM matrix and as a bridge to bond VMT with EPDM matrix. The influence of the MAV content and MA on the morphology and mechanical properties of the EPDM/MAV nanocomposites were investigated.

## **EXPERIMENT**

## Materials

The source vermiculite with a cation-exchange capacity (CEC) of 260 mequiv / 100 g was purified and screened by a 325-mesh sieve. EPDM was supplied by Yangzi Petrochemical (Nanjing, China) with an ethylene content of 70%, ENB type and  $ML_{1+4}$  100°C = 70. The maleic hydride (MA) and benzoyl peroxide (BPO) were supplied by Shanghai Chemical Reagent (Shanghai, China) and purified by recrystallization. Other reagent grade chemicals were used without further purification.

#### Preparation of MA-Delaminated VMT

Approximately 50 g of the pristine vermiculite was introduced into 2 L of a 1 M HCl solution in a beaker at room temperature. The resulting slurry was magnetically stirred for 6 h. The pH of the slurry was adjusted to 3.0-4.0. The vermiculite was then separated by filtering and washed thoroughly with distilled water several times until the filtrate had a pH value of 7.0. Following washing, the obtained solid material was dried at 200°C overnight. The final product after grinding was a fine powder with as-received color. The delamination process of vermiculite was controlled and monitored by X-ray diffraction. The acid-delaminated vermiculite was then further treated with MA. To a 250-ml flask were charged 50 g of MA, 50 g of acidtreated vermiculite, and 100 ml of acetic acid. The slurry was magnetically stirred for 12 h. The resulting slurry was dried in a rotary evaporator at 60°C and subsequently dried in an oven at 70°C for 24 h under vacuum. The final MA-intercalated vermiculite in the form of fine powder was screened by a 325-mesh sieve and kept in a desiccator.

### Preparation of Nanocomposites

Nine g EPDM and 1 g MAV were melt-mixed in a HAAKE Rheometer RC90 (Haake, Germany) for 5 min at 90°C and a rotor speed of 136 rpm, followed by the addition of 0.1 g BPO, the mixing lasting another 5 min. The resultant mixture was pressed into sheets on a two-roll mill at ambient temperature and was compression-molded at 175°C for the optimum cure time to yield a rubber vulcanizate. The resultant nanocomposites are termed EPDM/

MAV-5 throughout this article, where 5 is the weight percent of montmorillonite. The nanocomposites composed of 8.5 g EPDM and 1.5 g MAV or 8 g EPDM and 2 g MAV were prepared as widely described and termed EPDM/ MAV-7.5 and EPDM/MAV-10, respectively.

#### Characterization

X-ray diffraction measurements were made directly from VMT and MAV powders. The dispersion of clay in polymer matrix was evaluated with X-ray diffraction measurements carried out on films. All XRD measurements were performed on a X'TRA XRD (ARL, Switzerland) with Cu K $\alpha$ radiation (1.54Å) and the patterns were recorded in the reflection mode for 2  $\theta = 1-10^{\circ}$  using a scanning speeding of 2°/min. The basal spacing of the VMT was estimated from the (001) peak in the XRD pattern. The morphology of EPDM/MAV nanocomposites was performed with a JEM-200 CX transmission electron microscope (JEOL, Japan) using 200 kV accelerating voltage. Samples were embedded in epoxy resin, cured at 60°C overnight, and subsequently microtomed at room temperature into ultrathin slices (<100 nm thickness) using a Reichert-Jung Ultracut E microtome. Sections were collected with 300-mesh copper grids and were observed without any further modification or coating. The morphology of the break surface of tensile samples was observed with X650 scanning electron microscopy (Hitachi, Japan). The operation voltage was 20 kV. All the samples were gold-coated by means of an IB3 (Eiko Engineering, Japan) sputtering apparatus before observation.

The thermogravimetric analysis was done on a TA 2100-SDT 2960 (Perkin Elmer, Norwalk, CT) with a temperature ramp of 20°C/min under N<sub>2</sub> atmosphere from 25–800°C. The dynamic mechanical thermal analysis was carried out on a DMTA V (Rheometric Scientific, Ithaca, NY) in the tension mode using rectangular samples. The sample was subjected to a cyclic tensile strain with amplitude of 0.2% at frequency of 10 Hz and a static force of 0.1 N was used. The temperature ramp was 3.0°C/min and the scanning range was from  $-90^{\circ}$ C to 50°C.

The tensile strength, elongation at break, and modulus were measured using an Instron-4200 (Instron, UK) at a crosshead speed of 500 mm/min using the ASTM D 412 method. The result reflects an average of five specimens and all the mechanical properties were tested at 23°C.

## **RESULTS AND DISCUSSION**

### Choice of Surfactants

In the previous preparation of layered silicate nanocomposites, refined clay is routinely first treated by exchanging metal cations, usually Na ions, absorbed on the negatively charged surface of the platelets with onium ions, especially quaternary ammonium salts surfactants. The larger quaternary ammonium salts, applied from aqueous alcohol solution in which the clay platelets are suspended colloidally, force the plates into a larger spacing. Among the surfactants adopted during the preparation of organophilic clay, not all are equally effective because of the strong impact of thermodynamics. Some are effective in opening up the gallery, but they may not introduce high interfacial interactions with the polymer matrix—for example, quaternary ammonium salts. Others may not open up the gallery at all individually, while they may lead to strong attraction between the interfaces of platelet layer and polymer matrix.

First of all, vermiculite should be delaminated by proper thermal treatment and suitable surfactants to have an appropriately larger interlayer space for successful intercalation of the long chain of polymers [11]. In the present work, MA was selected to open the interlayer space of VMT; at the same time, it was adopted to introduce stronger interactions between EPDM and VMT, and then to increase the potential binding energy of the whole system by the introduction of polar groups such as -COOH along the gallery of silicate. On the other hand, according to the self-consistent field (SCF) depicted by Singh and Balazs [12], the enhanced miscibility between the organically modified clay and the polymers with higher number of branches is primarily due to the compactness of the macromolecules. EPDM can be blended with MA to form a comb chain in the presence of BPO. The radius of gyration of the polymers decreases as the number of branches increases, and the polymer can more easily interact with and interpenetrate the VMT layer.

Additionally, according to the lattice-based mean field theory depicted by Vaia and Giannelis [13], the outcome of polymer intercalation is generally determined by the interplay of entropic and enthalpic factors. A favorable energy decrease is associated with the establishment of many favorable polymer/surface polar interactions. The enthalpy of mixing can thus be rendered favorable by maximizing the magnitude and number of favorable polymer/surface interactions while minimizing the magnitude and number of unfavorable apolar interactions between the polymer and the aliphatic chains introduced along the modified layer surfaces. The introduction of MA along the platelet surfaces slightly changes the interlayer environment and increases the favorable polar interactions between EPDM and VMT. Then the intercalation of EPDM into the interlayer will become more thermodynamically favorable.

#### Structure and Morphology

The mica-type silicate of vermiculite possesses a layered structure. Each layer of VMT consists of octahedrally coordinated cations (typically Mg, Al, and Fe) sandwiched by tetrahedrally coordinated cations (typically Si and Al). The isomorphous substitution of Si<sup>4+</sup> by Al<sup>3+</sup> leads to a net negative surface charge that is compensated by an interlayer of exchangeable hydrated cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and H<sup>+</sup>). Adjoining layers are held together by a combination of electrostatic and van der Waals forces. For layered VMT, various methods have been used to delaminate the layered



FIG. 1. X-ray diffraction patterns of VMT; (a) pristine VMT, (b) aciddelaminated using 1 M HCl followed by drying at 200°C overnight, (c) MA-treated VMT (MAV).

structure. For example, VMT can be pretreated with surfactants such as alkyl ammonium ions or reactive organic compounds to produce an organo-clay, by ion-exchange methods, or by direct heating in a reactive vapor phase [14, 15].

In this work, an acid treatment route was used to delaminate vermiculite partially before the incorporation of the MA swelling agent. For monitoring the interlayer space after treatment, the XRD patterns of as-received VMT subjected to HCl and MA treatments are depicted in Fig. 1. The *d*-spacings of the VMT before and after treatment were calculated using Bragg's equation according to the angle of 001 diffraction peak (2d sin  $\theta = \lambda$ , where  $\lambda$  corresponds to the wave length of the X-ray radiation used in the diffraction experiment, *d* is the spacing between diffraction lattice planes, and  $\theta$  is the measured half diffraction angle or glancing angle).

It can be found that after acid treatment the  $d_{001}$  of pristine VMT have increased from 1.44 nm to 3.40 nm. This is because the hydrated silicate can be delaminated by proper thermal and acid treatment. To further delaminate the VMT layers, partially delaminated VMT was exposed to a mixed MA and acetic acid solution and stirred for 12 h. XRD traces of MAV (Fig. 1c) indicate the absence of diffraction peaks, which clearly reveals that the VMT is further delaminated, according to the literature [16]. The result implies that the gallery spacing of VMT is larger than 4 nm. MA can easily enter the galleries of acid-treated VMT because solvent (acetic acid) can act as a carrier to transport MA into hydrophilic VMT.

Figure 2 shows that all the nanocomposites with MAtreated VMT have no evident diffraction peaks in the measured angle scope. According to the literature [7, 11, 17], the absence of the characteristic  $d_{001}$  diffraction peak of clay is strong evidence for the formation of exfoliated or disor-



FIG. 2. X-ray diffraction patterns of EPDM/MAV nanocomposites. A feeble peak (black arrow) indicates that some layer structure of the exfoliated VMT rearranged to a minor extent in the EPDM/MAV-10 nanocomposite.

dered nanocomposites. As far as exfoliated or disordered structure of VMT nanocomposites is concerned, no more diffraction peaks are visible in the XRD patterns either because of much too large spacing between the layers (i.e., exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposites do not present ordering anymore. A different situation is observed in the XRD patterns of EPDM/MAV-10, where a feeble peak (black arrow) is visible at 2  $\theta = 6.12^{\circ}$  corresponding to a basal spacing of 1.44 nm, and this indicates that some layer structure of the exfoliated VMT is rearranged to a minor extent in EPDM/MAV-10 nanocomposite, which was encountered at higher filler content.

XRD data alone gives a partial picture of the clay distribution. In exfoliated nanocomposites, the dimension and the distribution of layers could be very variable and a complete characterization of the nanocomposites morphology requires also a microscopic investigation. Typical TEM micrographs of an EPDM/MAV-7.5 nanocomposite are shown in Fig. 3. In the micrographs the brightfield belongs to the EPDM matrix or blank and the dark lines are the transverse sections of silicate platelets. It can be seen that all the MAV are exfoliated and dispersed uniformly in the EPDM matrix; this result is consistent with the conclusion from XRD. From Fig. 3, the VMT layer exhibits a thickness of 1-2 nm and a length of about 200 nm, indicating that the VMT layers have a very large aspect ratio. However, the average thickness of VMT platelets in other nanocomposites [3, 11, 17, 18] is also somewhat higher than that of a single clay layer, which should be about 1 nm [19]. There are two possible reasons for this discrepancy. One possibility is that the platelets appear in the image to be larger than they actually are due to inaccurate focusing in TEM. Another possibility is that the microtoming direction is not perfectly perpendicular to the surface of the platelets, so the image is of a tilted platelet that appears to be thicker than it actually is. Additionally, from Fig. 3b it is evident that the spacing between the layers is  $\geq 10$  nm, which is consistent with XRD.

Figure 4 shows a typical SEM micrograph of the break surface of tensile samples of EPDM/MAV-7.5 nanocomposite. Exfoliated VMT layers (black arrows) can be readily seen in the SEM micrograph and dispersed uniformly in the EPDM matrix; this result is consistent with the conclusion from XRD and TEM. A micrograph of the sample reveals that the interface between the individual VMT layers and EPDM is not clear. This means that the MAV layers could be well dispersed in EPDM matrix and that the EPDM matrix could contact well with VMT through the formation of a ternary molecular structure (VMT-MA-EPDM) as a result of the presence of MA. It should be noted that both the average thickness and the length deduced from the SEM photomicrographs are somewhat higher than those observed from the corresponding TEM micrographs. This is because the resolution of electron microscopes depends on the electron wavelength and aberration of the lenses. TEM generally exhibits a much higher image resolution than SEM because the magnetic lenses of TEM have lower spherical aberrations [11]. Moreover, TEM is operated at higher voltages, 200 kV, compared to SEM, at 20 kV in this work. This implies that the wavelength of electrons is shorter in TEM than in SEM.

From the results of XRD, TEM, and SEM, it can be concluded that EPDM could be blended with MAV to form exfoliated EPDM/MAV nanocomposites, which constitutes a ternary molecular structure (VMT-MA-EPDM) in the presence of benzoyl peroxide (BPO). In such a structure, MA serves as a modifying additive for the EPDM matrix and as a swelling agent for VMT. Then the long molecular chains of the EPDM are easy to diffuse into the galleries of VMT and the homogeneous dispersion of the VMT layer in the EPDM matrix is successfully realized. A conceptual scheme of forming a process of exfoliated EPDM/MAV nanocomposites is depicted in Fig. 5. In such a compatible structure, grafted MA acts as a vulcanizing agent for the EPDM matrix and as a center or a bridge to bond VMT and EPDM together. To further confirm the excellent properties of exfoliated EPDM/MAV nanocomposites constituted of a ternary molecular structure (VMT-MA-EPDM), the thermal and mechanical properties of nanocomposites were investigated and are discussed as follows.

#### Thermal Properties

As reported by many other researchers, the introduction of silicate can improve the thermal properties of the polymer matrix [20]. In this work, the thermogravimetric analysis of the EPDM/MAV nanocomposites was carried out from room temperature to 800°C. In order to study the degradation thoroughly, the onset temperature ( $T_d$ ) of the degradation processes and the temperature of the maximum



FIG. 3. Typical TEM micrographs of EPDM/MAV-7.5 nanocomposite showing (a) formation of exfoliated VMT layers in the nanocomposite and (b) enlarged image of exfoliated VMT layers.

degradation rate  $(DTG_{max})$  were derived and are shown in Table 1.

From Table 1 it can be seen that the onset temperature of EPDM/MAV-7.5 is 16.2°C higher, and the temperature of maximum degradation rate (DTG<sub>max</sub>) of EPDM/MAV-5 is 4.4°C higher compared to EPDM. Resistance to thermal degradation is improved when the VMT content is increased to 7.5 wt%. The increase in  $T_d$  and  $DTG_{max}$  result from the fact that nanosized VMT layers, 1-2 nm thick and about 200 nm long, are able to sustain high temperatures and to retard the heat diffusion into the EPDM matrix. With a further increase VMT content, no further increases in the T<sub>d</sub> and DTG<sub>max</sub> of the composites were observed. One possibility is that with high VMT content, for example 10%, VMT coagulated in the EPDM matrix and could not disperse very well; this result is consistent with the conclusion from XRD (Fig. 2c). Another is that the acid-pretreated VMT contains unreacted MA when the VMT content is  $\geq 10$  wt%.

The dynamic mechanical thermal analysis is a good

method to detect the change in glass transition temperature  $(T_g)$  and to examine the degree of filler-matrix interaction of the EPDM/MAV nanocomposites. It can be seen that the addition of MAV results in an enhancement of  $T_g$  (Table 1). The enhancement in  $T_g$  is most manifest in the case of the EPDM/MAV-7.5 nanocomposite, which enhanced from -35.014 to -30.265°C. This slight shift to higher temperature might be explained by the mobility of EPDM molecular chains being restricted by the presence of VMT layers.

Figure 6 shows the effect of MAV on the storage modulus of the nanocomposites. It is evident from Fig. 6 that the storage modulus of EPDM/MAV is large than that of EPDM as a function of temperature due to the greater reinforcing effect of MAV. For example, the storage modulus at 25°C of EPDM/MAV-7.5 is 3 times higher than that of pure EPDM. This beneficial effect is believed to arise from an improvement in the compatibility between the VMT and EPDM matrix associated with an MA addition. Consequently, a ternary molecular structure of VMT-MA-



FIG. 4. Typical SEM micrograph of EPDM/MAV-7.5 nanocomposite. Black arrows indicate VMT layers.

EPDM with MA in the grafted EPDM as a center can develop in these nanocomposites (Fig. 5). Moreover, the ternary structure can promote the nanoscale dispersion of vermiculite within the EPDM matrix, then the storage modulus increases significantly upon formation of the nanocomposites. The increase in storage modulus is most manifest in the case of EPDM/MAV-7.5; this is consistent with the conclusion above.

#### Mechanical Properties

Exfoliation of VMT in the EPDM matrix provided EPDM/MAV nanocomposites with outstanding mechanical properties, as shown in Table 2. It can be seen that, relative to the EPDM matrix, all of the nanocomposites show high enhancement in tensile, tear, and modulus properties. Compared with the EPDM matrix, the nanocomposite from EPDM/MAV-7.5 show the highest tensile strength, enhanced by about 107%, which is due to nanoscale dispersion of VMT within the EPMD matrix. With a further increase of clay content, the tensile strength and the elongation at autobreak of the nanocomposites decreased, but the Young's modulus increased slightly. The increase in the mechanical properties for the nanocomposites were apparently caused by the addition of MA-intercalated VMT. In conventional composites, however, the interfacial bonding between the matrix and the reinforcing materials is relatively poor. Thus, MA is used to improve the interfacial adhesion between them. On the other hand, the maleic anhydride functional group of EPDM/MAV nanocompos-



FIG. 5. Conceptual figure of forming process of exfoliated EPDM/MAV nanocomposites.

TABLE 1. Thermal properties of EPDM and EPDM/MAV.

|              | VMT<br>content (%) | $T_d$ (°C) <sup>a</sup> | DTG <sub>max</sub><br>(°C) <sup>a</sup> | $\underset{(^{\circ}\mathrm{C})^{\mathrm{b}}}{T_{g}}$ |
|--------------|--------------------|-------------------------|---|---|
| EPDM         | 0                  | 445.186                 | 478.461                                 | -35.014   |
| EPDM/MAV-5   | 5%                 | 456.845                 | 482.834                                 | -30.313   |
| EPDM/MAV-7.5 | 7.5%               | 461.381                 | 482.117                                 | -30.265   |
| EPDM/MAV-10  | 10%                | 455.802                 | 480.645                                 | -30.641   |

<sup>a</sup>Determined by thermogravimetric analysis (TGA).

<sup>b</sup>Determined by dynamic mechanical thermal analysis (DMTA).

ites tends to exfoliate the galleries of VMT, leading to nanoscale dispersion of reinforcement within the polymer matrix. The uniform dispersal of the MAV nanolayers in the EPDM matrix is considered to form a physical barrier against a growing crack, which leads to the increase in the resistance to tearing. These observations indicate that the exfoliation of VMT in the EPDM matrix can offer the nanocomposites effective enhancement in toughness and strength as well as stiffness.

## CONCLUSIONS

Exfoliated EPDM/MAV nanocomposites can be readily prepared by blending with MA-treated VMT to form a ternary molecular structure (VMT-MA-EPDM) in the presence of benzoyl peroxide (BPO). Maleic anhydride (MA) acts both as the intercalation agent for VMT and as a vulcanizing agent for the EPDM matrix. It also acts as a compatibilizer for the EPDM and VMT phases. The absence of VMT reflections in the XRD patterns demonstrates that the EPMD/MAV exhibit nanocomposite characteristics. The TEM and SEM observations are consistent with the XRD results. From DMTA results, it can be seen that a strong rubber–filler interaction in the nanocomposites is manifested in the measured temperature range and VMT



FIG. 6. Storage modulus of EPDM and EPDM/MAV nanocomposites.

TABLE 2. Mechanical properties of the EPDM/MAV nanocomposites.

|              | VMT<br>content<br>(%) | Stretch<br>strength<br>(Mpa) | Elongation at<br>autobreak<br>(%) | Modulus<br>(Aut Young)<br>(Mpa) |
|--------------|-----------------------|------------------------------|-----------------------------------|---------------------------------|
| EPDM         | 0                     | 2.905                        | 2,165.3                           | 1.851                           |
| EPDM/MAV-5   | 5%                    | 4.361                        | 2,494.2                           | 1.942                           |
| EPDM/MAV-7.5 | 7.5%                  | 5.998                        | 2,225.2                           | 2.063                           |
| EPDM/MAV-10  | 10%                   | 3.703                        | 1,978.1                           | 2.473                           |

addition increases the  $T_g$  of nanocomposites. There is some enhancement in degradation behavior between the nanocomposites and the EPDM matrix. Finally, the tensile tests show that the tensile modulus and strength of the nanocomposites tends to increase compared to EPDM.

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