Synthesis of EPDM/Organoclay Nanocomposites: Effect of the Clay Exfoliation on Structure and Physical Properties

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A B S T R A C T

The preparation of ethylene propylene diene terpolymer (EPDM)/organoclay nanocomposites was studied by melt blending method. The maleic anhydride modified EPDM oligomer (EPDM-MA) was used as a compatibilizer. The effect of organoclay on structure of nanocomposites was evaluated by X-ray diffraction (XRD). The absence of basal plane peak in XRD results and homogeneously dispersed clay platelets in EPDM matrix, which is shown by TEM photograph suggests that the EPDM clay nanocomposits are exfoliated. The mechanical and thermal properties of nanocomposites were examined to evaluate the influence of the organoclay on the physical properties. The results show remarkable improvement relative to that of EPDM without clay. To prepare EPDM-clay nanocomposites by a straightforward method, a second process was implemented. It was found that the properties of nanocomposites prepared by both methods are nearly the same; however the second method has lower cost and it is industrially more practical.

INTRODUCTION

Development of the polymer-clay nanocomposites is one of the latest evolutionary steps of the polymer technology. Currently, the polymer family of nanocomposites has attracted the attention of many researchers; Hasegawa et al. [1] reported a novel compounding process using Na-montmorillonite water slurry for preparation of nylon 6 nanocomposites. Kornmann et al. [2] have studied the effect of curing agent on synthesis of exfoliated epoxy clay nanocomposites and Fu et al. [3] pre-

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pared exfoliated polystyrene nanocomposites by bulk polymerization. As a result of this nanometer size effect, generally very large relative surface area and strong interaction with polymer matrix, nanocomposites exhibit superior properties compared to both conventional composites and unreinforced bulk polymer including: mechanical properties [4-6], barrier properties [7], flame retardancy [8,9], thermal stability [10] and chemical and dimensional stability [11,12].

The most commonly used clay is the smectite mineral group such as montmorillonite (MMT). Smectites are available mineral class for industrial applications because of their high cation exchange capacities, surface areas, surface reaction and adsorption properties. Their structures consist of two silica tetrahedral sheets to an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. Stacking of the layers of ca. 1 nm thickness by a weak dipolar force leads to interlayer or galleries between the layers, the galleries are normally occupied by cations such as K^+, Na^+, Ca^+, Mg^+, and Cs^+ by which it is easy to form the organosilicate by an alkylammonium ion-exchange reaction [13]. The organosilicate can be broken down into their nanoscale building blocks and uniformly dispersed in the polymer matrix. When the nanoparticles are dispersed in the polymer matrix, two types of nanocomposite structures can be obtained [14]. Intercalated nanocomposites are formed when there is a limited inclusion of polymer chain between the clay layers with a corresponding small increase in the interlayer spacing of a few nanometers. On the other hand, exfoliated structures are formed when the clay layers are well separated from each other and individually dispersed in the continuous polymer matrix. Because exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart, an exfoliated structure is more desirable in enhancing the properties of the nanocomposites.

Ethylene propylene diene terpolymer (EPDM) is a synthetic rubber with wide application area such as automobile parts, footwear, electrical field, roofing barriers and sporting goods. However, it is incompatible with polar organophilic clay to prepare products having desired properties because EPDM does not include any polar group in its backbone [15]. Recently, Toyota research groups reported a novel approach to prepare nonpolar polymer clay hybrids by using a functional

oligomer [16,17]. So far, there are very few studies on formation of EPDM-clay nanocomposites. Usuki et al. [18] prepared EPDM/clay hybrids via vulcanization process using some special vulcanization accelerators; they concluded that the intercalation of the EPDM molecules into clay galleries occurred during the time of mixing roll and vulcanization process. Chang et al. [19] treated sodium MMT with octadecylammonium ion and subsequently with a low molecular weight EPDM liquid, and then mixed the OMMT with EPDM via a simple melt compounding process. As an extension to their studies, in this effort the EPDM-clay nanocomposites have been prepared by melt blending techniques, using two different approaches and a maleic anhydrid grafted EPDM oligomer (EPDM-MA) to prepare exfoliated nanocomposites. There are two main goals in this paper. The first aim is to study the miscibility effect of the oligomer on the dispersibility of the organoclay in the EPDM matrix and second one is to investigate the effect of organoclay on the mechanical properties such as tensile strength, tensile modulus, elongation-at-break and hardness of EPDM nanocomposites.

EXPERIMENTAL

Materials

Maleic anhydrid grafted EPDM oligomer (EPDM-MA) as compatibilizer (EPDMg002) was obtained from Hu Zhou Plastic Co., Ltd (Hu Zhou, China). Pure sodium montmorillonite (Na^+-MMT) (Kunipia-F) with a cation-exchange capacity (CEC) of 119 meq/100g was supplied by Kunimine Mining Ind. Co. (Tokyo, Japan), and octadecylamine purchased from Fluka was used as an organic modifier of MMT. The EPDM used (J-3062E) of ENB type was obtained from Jilin Chemical Ind. Co., Ltd (Jilin, China). All chemicals were used without further purification.

Synthesis of Organically Modified Montmorillonite

Organoclay was prepared according to the reported method [16]. Octadecylamine, 4.8 g, (115 mmol) and con. HCl (1.8 mL) were dissolved in 400 mL of 80 C de-ionized hot water and 12 g Na^+-MMT was dispersed in 600 mL hot water. Then, the first solution was poured in MMT-water and it was vigorously stirred for

1 h. The white precipitate was filtered in a suction filtration and washed several times with de-ionized hot water to remove chloride ions completely and then it was dried in a vacuum oven at 80 C for 14 h.

Preparation of EPDM Organoclay Nanocomposites
Different combinations of organoclay and EPDM were prepared through melt blending method (termed indirect method). First, maleic anhydride-grafted EPDM oligomer (EPDM-MA) and organoclay powder were dry mixed by shaking in a bag. This mixture was melt-mixed at 150 C using a twin-screw blender with screw rotational speed of 90 rpm and mixing time of 15 min to yield organoclay intercalated EPDM-MA. In the second stage, the pellets of EPDM and organoclay intercalated EPDM-MA were melt blended at 150 C using twin-screw blender for 15 min to give the EPDM-organoclay nanocomposite. The compositions of EPDM-CN are shown in Table 1.

For the evaluation of the effect of EPDM-MA as a compatibilizer, the composite of EPDM (100 phr) and organoclay (3 phr) without EPDM-MA was also prepared.

The EPDM-CNs (100 phr) were sequentially mixed with zinc oxide (5 phr), stearic acid (1 phr), vulcanization accelerator [M (2-mercapto benzothiazole, 0.5 phr) and TMTD (tetramethyl thiuram disulphide, 1.5 phr)] and sulphur (1.5 phr) by using a mixing roll. Vulcanized EPDM clay hybrids were press-moulded at 150 C for 30 min to yield rubber sheets of 340 1 × 150 w × 2 t mm dimensions.

In order to obtain a facile approach to prepare nanocomposites by melt blending process, a different way (termed direct method) was implemented in this work. Three components of EPDM (100 phr), EPDM-MA (20 phr) and organoclay (5 phr) were dry mixed together by shaking them in a bag and then this mixture was melt-blended in one stage at 150 C for 15 min by using a twin screw blender to yield nanocomposite. The nanocomposite was vulcanized under above mentioned conditions.

Characterization and Measurements
Dispersibility of the organoclay in the polymer matrix was evaluated by X-ray diffraction (XRD). XRD Patterns were recorded by using a Phillips X Pert X-ray generator with CuKα radiation at 40 KV and 40 mA. The diffractograms were scanned in 2θ range from 1 to 10 at a rate of 2.4 /min. The tensile measuring test was carried out with universal tensile tester (Model DCS-5000, Shimadzu Co.) at 25 C; the head speed was 500 mm/min, according to ASTM D412 specifications. Hardness was measured by using a shore-A hardness instrument (LX-A, Shanghai Liuling factory, China). All mechanical measurements were carried out several times and the data obtained were averaged. The dynamic modulus of EPDM-CN5 was measured by using a dynamic mechanical analyzer (DMTAV, Rheometric Scientific Co.). The sample was subjected to a cyclic tensile strain with different amplitudes at a constant frequency of 1 Hz. For temperatures within the range of -100 C to -20 C, an amplitude of 0.05% and for the range of -20 C to 100 C an amplitude of 0.2% were used. The temperature was increased at the heating rate of 2 C/min. Thermogravimetric analysis (TGA) was performed under argon gas at a heating rate of 10 C/min with STA-499 TGA instrument (Netzsch Co.). The experiments were carried out from 30 C to 600 C.

The melt mixing was carried out with using a twin-screw blender model RM-200, manufactured by Harbin University of Science and Technology (China), with chamber size of about 40 cm^3.

RESULTS AND DISCUSSION

To obtain the exfoliated structure of nanocomposites, the organclay was used as nanoparticles and the EPDM-MA was used as compatibilizer. The experimental conditions were fixed by setting the temperature at 150 C, mixing time of 15 min and the rotational speed of blender was adjusted at 90 rpm.
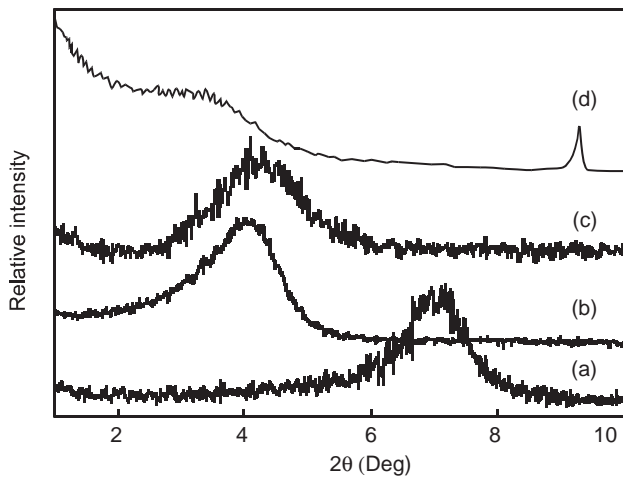
Organo-modification of MMT
XRD is a fast technique to detect the change of the interlayer distance of silicate layers. The XRD patterns of

Table 1. Composition of EPDM-CN.

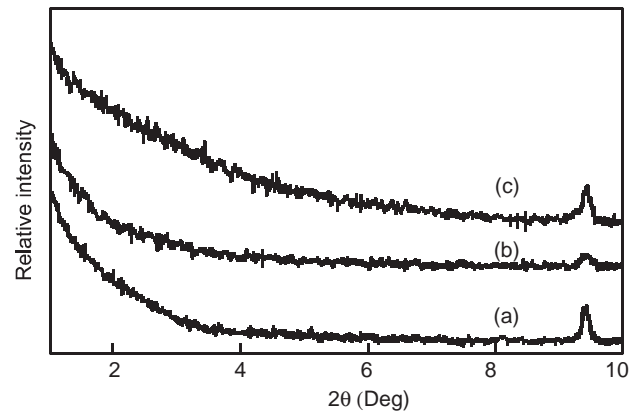| Sample code / Composition	EPDM-CN2	EPDM-CN5	EPDM-CN8	EPDM-CN10
EPDM (phr)*	100	100	100	100
EPDM-MA (phr)	20	20	20	20
Organoclay (phr)	2	5	8	10

*phr (part per hundred part of rubber by weight).

Figure 1. XRD Patterns of (a) pure clay (MMT)(2g), (b) organoclay (2g); (c) EPDM + MMT (3 phr) + and (d) organoclay (3 phr) + EPDM-MA.

Figure 2. XRD Patterns of (a) EPDM-CN5; (b) EPDM-CN8; and (c) EPDM-CN10.

pure clay (MMT) and organoclay are shown in Figure 1 (a,b). MMT has characteristic diffraction peak (Figure 1a) corresponding to the (001) plane at 7.1 (1.24 nm), but for organoclay the interlayer spacing (Figure 1b) has increased up to 4 (2.19 nm). This obviously indicates that the alkyl ammonium chains were intercalated between the layers of clay and, therefore the interlamellar spacing of clay is enlarged. The basal spacing of the silicate layers, *d*, was calculated according to Bragg s equation, $\lambda = 2d \sin \theta$.

Characterization of Nanocomposites by XRD
XRD is an effective way to characterize the formation of a nanocomposite. In an immiscible mixture, the gallery height of clay, in terms of its d-spacing, should be virtually identical to that of the pristine clay; if a nanocomposite is formed, the d-spacing must increase. Two cases are possible, a peak is seen at larger d-spacing than in the pristine clay, indicating an intercalated structure, or no peak is seen, which may indicate either an exfoliated structure or disordering of the clay layers.

Figure 1c shows the XRD patterns of the mixture of organoclay with EPDM. The result clearly shows that the (001) plane peak of the organoclay does not shift to lower angle at all, which indicates that EPDM does not intercalate into the galleries of organoclay, because EPDM does not include any polar group in its backbone and silicate layers of clays, even modified by non-polar alkyl groups are polar and incompatible with EPDM.

The XRD pattern of composite of EPDM-MA with organoclay (Figure 1d) shows that the 001 plane reflections shift to angles smaller than that of organoclay, which indicates that EPDM-MA intercalated into layered silicate of clay and expand the basal spacing of organoclay. The strong hydrogen bonding between maleic anhydride group (or COOH group which is caused by the hydrolysis of the maleic group) and oxygen group of the silicate can produce the driving force necessary for the intercalation [20]. The interlayer spacing of the clay as well as its compatibility with polymer are increased, so the clay galleries could be easily intercalated with the EPDM, the basal spacing between nanolayers of silicates are more increased, and as a result, the peak of XRD pattern of EPDM nanocomposites is disappeared (Figure 2).

The XRD patterns of the EPDM-CNs with various amounts of organoclay are shown in Figure 2. No obvious diffraction peak is observed in EPDM-CN5, EPDM-CN8, and EPDM-CN10, the disappeared peak of 001 plane in XRD pattern indicates that each layer of the clays is dispersed homogeneously in EPDM matrix and exfoliated nanocopmposites is formed [1,2], although a slight amount of unexfoliated layers still exists but because of the very small amount of unexfoliated layers, their peaks are not appeared in XRD pattern. The diffraction peak at 9.5 , which was also being observed in Figure 1, is related to EPDM-MA.
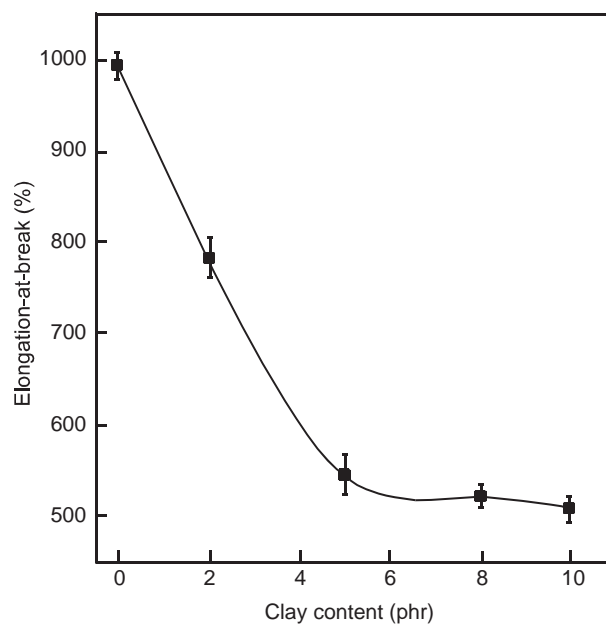
Mechanical Properties
The mechanical properties of EPDM-clay hybrids are measured and summarized in Figures 3-6. Greater
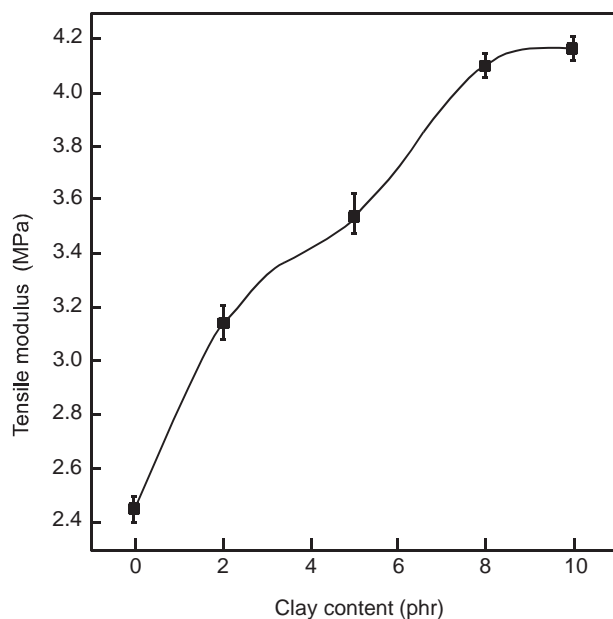
Figure 3. Effect of clay content on tensile modulus of EPDM-CNs.

**Figure 5.** Effect of clay content on elongation-at-break of EPDM-CNs.

improvements in tensile strength, tensile modulus and hardness are clearly observed for the EPDM-clay hybrids. Figure 3 shows the tensile modulus of EPDM-clay hybrids increase rapidly with increasing clay content. For example, the tensile modulus of EPDM with 10 phr organoclay content has been 70% improved more than that of EPDM without any clay. The large

improvement in the tensile modulus can be attributed to the more uniformly dispersion of the nanoparticles of the layered silicates in the matrix of the polymer.

The tensile strength also increases sharply with increase in the clay content (Figure 4). The tensile strength of EPDM with 5 phr clay content has improved by 130%, which is higher than that of EPDM without any clay, but with high clay content, the tensile
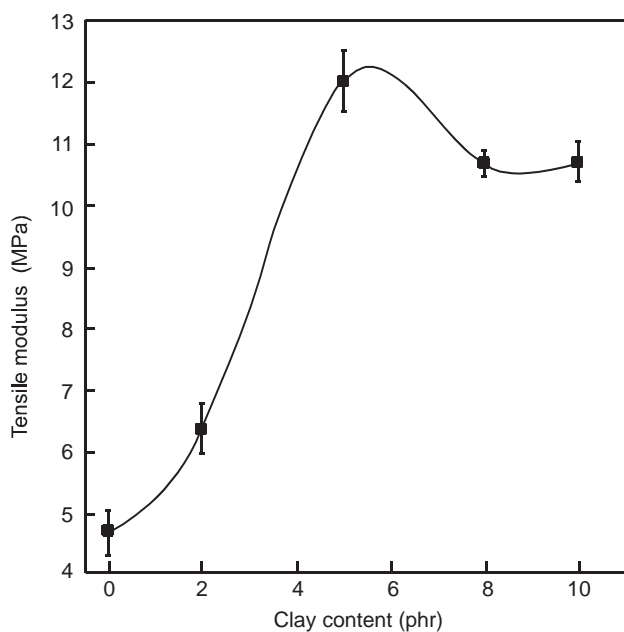
Figure 4. Effect of clay content on tensile strength of EPDM-CNs.
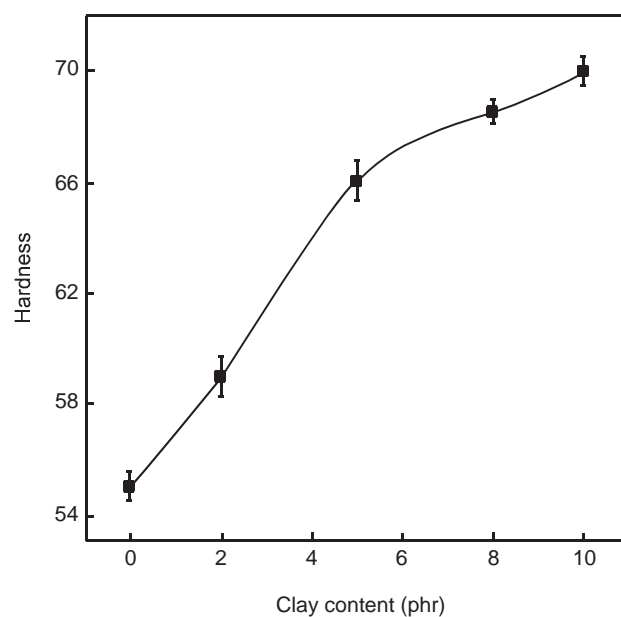
Figure 6. Effect of clay content on hardness of EPDM-CNs.

Table 2. Thermal properties of EPDM-clay nanocomposites.

| Sample	EPDM	EPDM-CN2	EPDM-CN5	EPDM-CN8	EPDM-CN10
Decomposition temperature (C)	474.8	478.2	479.4	479.4	480.1

strength slightly decreases. The enhancement in tensile strength is directly attributed to the dispersion of nanosilicate layers in the EPDM matrix and strong interaction between EPDM and clay, the lower tensile strength above 5 phr clay lodging can be attributed to inevitable aggregation of the silicate layers in high clay content.

The elongation-at-break of EPDM nanocomposites decreases with increasing the clay content (Figure 5). This may be attributed to the fact that ductility decreases when stiffness is increased by reinforcement.

Figure 6 shows the hardness of EPDM clay hybrids with different clay loadings. Addition of clay showed a remarkable increase in hardness. The uniformly distributed exfoliated platelets improved the stiffness of EPDM-clay hybrids. Presence of these stiff clay platelets and entanglement of polymer chains made the EPDM nanocomposites harder.

Dynamic Mechanical Analysis Measurements

The dynamic mechanical analysis (DMA) was recorded to study the effect of silicate nanolayer on the thermo-mechanical properties of EPDM clay nanocomposites. The storage modulus and the values of tan δ of EPDM and EPDM-CN5 as a function of temperatures are shown in Figure 7. Figure 7 a shows the storage modulus of the EPDM nanocomposite in comparison with unfilled EPDM; the EPDM-CN5 exhibits higher storage modulus than EPDM. Figure 7 b shows that the $δ_{max}$ of the EPDM-CN5 was decreased relative to that of EPDM at T_g, and also the T_g of EPDM-CN5 shifted toward a higher temperature. The lower tan δ and the increasing of storage modulus of EPDM nanocomposite can be attributed to maximizing of the adhesion between the polymer and layer silicate surfaces because of nanometer size, which restricts segmental motion near the organic/inorganic interface. Because of the higher ethylene content (68.5-74.5 wt%) in the EPDM, the second peak around 20 C may be attributed
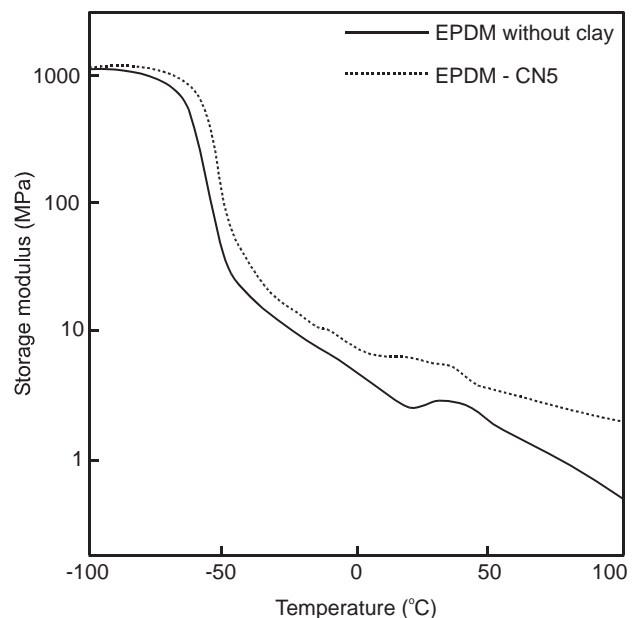
(a)
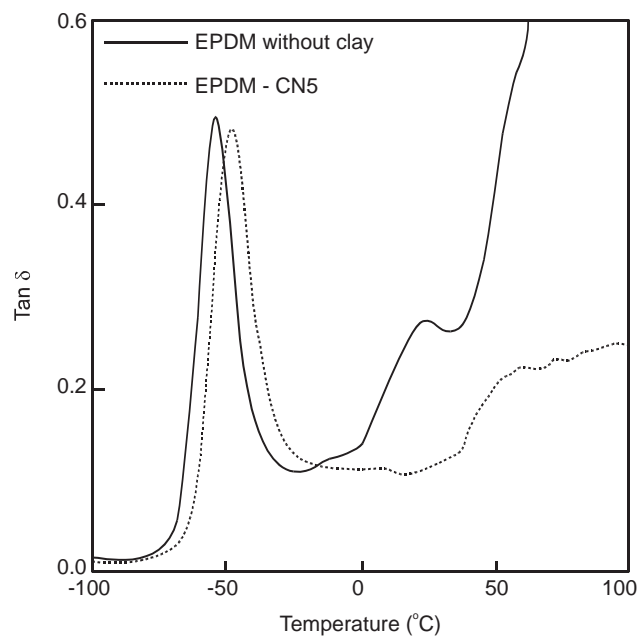
(b)

Figure 7. Dynamic mechanical spectra: (a) Storage modulus; (b) tan δ as a function of temperature for unfilled EPDM and EPDM-CN5.

Table 3. Mechanical properties of EPDM-CN5 prepared by (a) direct method (b) indirect method.

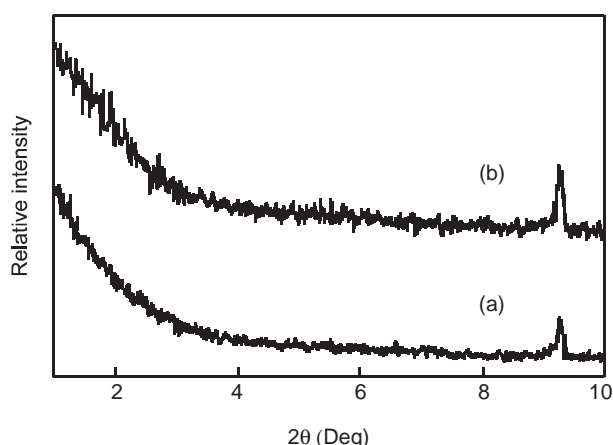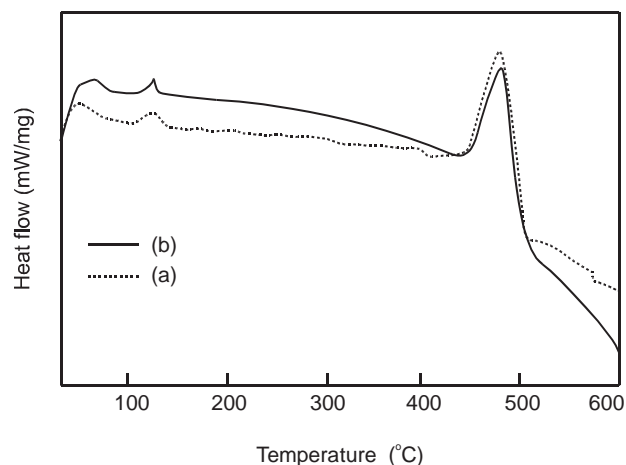| Method	Tensile strength (MPa)	Elongation-at-break (%)	Tensile modulus (MPa)	Hardness
Direct	12.06	550	3.41	68.5
Indirect	12.01	544	3.45	66.0

to the crystallization of EPDM in this temperature.

Thermal Properties of Nanocomposites

In order to study the effect of organoclay on the thermal behaviour of the nanocomposites, the thermal stability of EPDM-clay nanocomposites have been studied by TGA and the results are shown in Table 2. As it can be noticed, the thermal stability of EPDM-clay nanocomposites was increased slightly from 474.8 C to 480.1 C with increased clay loading. Thus, it can be said that nanocomposites formation has no significant effect on the thermal degradation of EPDM. The small increase of thermal stability is due to the presence of the clay nanolayers, which acted as barriers to minimize the permeability of volatile degradation products from matrix [20].

Investigation of Preparation Methods of EPDM Clay Nanocomposites

Direct and indirect methods were used to prepare EPDM-clay nanocomposites. The condition for both methods, including instruments, temperature and rotational speed were similar but the performance was difference. In these two methods, at first, the EPDM-MA oligomer intercalates between the layers of the clay

Figure 9. DSC Curves of EPDM-clay nanocomposites prepared with: (a) direct method and (b) indirect method.

through the strong hydrogen bonding between maleic anhydride group (or COOH group which is caused by the hydrolysis of the maleic group) and oxygen group of the silicate, so the interlayer spacing of the clay increases and the interaction of the clay to be weakened. Then, the intercalated clays with the oligomer disperse in the polymer matrix under strong shear action.

The results obtained from comparing two methods are shown in Figures 8, 9 and Table 3. Figure 8 shows the XRD pattern of EPDM-clay nanocomposites. There is no distinct (001) plane peak of the clay for two hybrids, indicating that in both methods the clay is exfoliated in polymer matrix. Figure 9 shows DSC curve of nanocomposites prepared by different methods. We can see that the temperature of maximum rate of mass loss of nanocomposites in both methods is nearly the same. Table 3 shows the mechanical properties of EPDM-CN5. From Table 3 we can see that the mechanical properties of nanocomposites obtained by both methods are almost same. Thus, it can be concluded that nearly similar product is obtained by both methods. However, the direct method has lower cost and it is also industrially more practical.

Figure 8. XRD Patterns of EPDM-clay nanocomposites prepared by: (a) indirect method and (b) direct method.

CONCLUSION

We prepared EPDM-CNs by melt blending, using two methods (direct and indirect). Exfoliated structure was observed by XRD analyses. Organosilicate has an important influence on mechanical properties of EPDM clay nanocomposites. By increasing the clay content; the tensile strength, tensile modulus and hardness have increased but elongation-at-breaks has decreased. Storage modulus and the values of tan δ of nanocomposites also increase. These enhancements are attributed to the more uniformly dispersed of nanoparticles of organoclay in polymer matrix.

ACKNOWLEDGEMENTS

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