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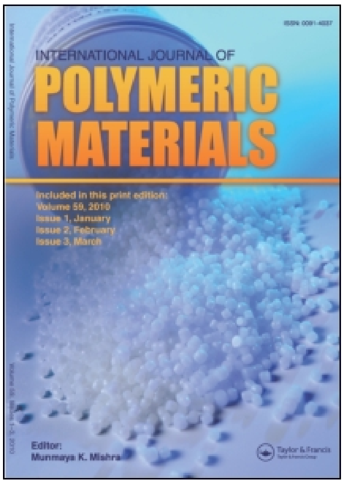

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Cure Characteristics and Mechanical Properties of Natural Rubber-Layered Clay Nanocomposites

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Cure Characteristics and Mechanical Properties of Natural Rubber–Layered Clay Nanocomposites

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The effect of interlayer distance of nanoclay on mechanical properties, cure characteristics, and swelling resistance of natural rubber (NR) in varying clay proportion were studied. X-ray diffraction results of nanocomposite with 10 phr of nanoclay showed the formation of an intercalated structure. The rate of vulcanization and maximum torque value of the nanocomposite are higher than the gum compound. Nanocomposites with clay having higher interlayer distance shows superior mechanical properties. Mechanical properties gradually increase with increase in clay loading up to 10 phr. A 50% increase in tensile strength and about 150% increase in modulus at 300% elongation were observed for the nanocomposite with 10 phr clay loading. Better barrier properties offered by the nanocomposites due to the presence of tortous path was confirmed by the Nielson's model.

Keywords: interlayer distance, nanoclay, natural rubber

INTRODUCTION

Polymer-layered clay nanocomposites are new hybrid polymeric materials with layered silicates in the form of sheets of one to several nanometers thick and hundreds of nanometer long. Due to the unique nanometer size dispersion of the layered silicates with high aspect ratio, high surface area, and high strength in the polymer matrix,

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nanocomposites exhibit improvement in properties even at very low volume fraction loading (1–5%) in the polymer matrix. The lower concentration of inorganic particles maintains clarity of the polymeric materials and allows conventional polymer processing operations. Rubber clay nanocomposites have drawn great attention in recent years since the application of rubber normally requires filler reinforcement [1–8]. The properties of rubber can be tailored by the addition of fillers of varying surface chemistry and aggregate size/aspect ratio to suit the application concerned. As the building blocks of a nanocomposite are of nanoscale they have larger surface area available for wetting by the polymer and therefore there are enormous interfaces between the two intermixed phases compared to usual microcomposites. The interfacial specific area can be of the order of a few hundred cm^2/gm of material and the effect of interfacial phenomenon is assumed to be noticeable on the bulk properties [9]. In addition to this the mean distance between particles is smaller because their size is small, favoring higher filler-filler interactions. Thus a better reinforcement is achieved by the incorporation of nano clay than the commercial clay. This reinforcement of rubbers is associated with the enhancement in modulus, failure properties such as tensile strength and tear strength, abrasion resistance, barrier properties, swelling resistance, and thermal properties.

Several types of morphology can occur when the polymer is mixed with layered silicates. (a) Immiscible, the polymer is incompatible with layered silicates and no polymer chains penetrate inside the gallery of layered silicate. (b) Intercalated, the polymer is compatible with the layered silicate and the polymer chains penetrate inside the gallery and expand the nanosheets to some extent, while the layered structure of the silicate is still in registry. (c) Exfoliated, the expansion of the layered silicate is so large that the interaction between the layers is not strong enough to keep the stack-like registry and association, and, ideally, the individual silicate layers are completely separated and dispersed in a continuous polymer matrix. The composite with the immiscible morphology is the traditional composite, whereas the composite with intercalated and exfoliated morphology are defined as nanocomposites.

The fundamental principle of polymer clay nanocomposite formation is that the polymer should penetrate into the intergalleries of the clay, so the space between the platelets or layered galleries of the silicate should be made accessible for the polymer chains. The layered silicates commonly used in polymer nanocomposites belong to the structural family known as the 2:1 montmorillonite (MMT). In the pristine state, MMT is made up of stack of platelets resulting in a much smaller aspect ratio in the range of 50–200. The layer thickness is around 1 nm and lateral dimensions of their layers may vary from 300 Å to several microns and even larger depending on the particular silicate. As the distance between the layers is less than 1 nm it does not allow the penetration of the polymer molecules therein. To support intercalation and exfoliation the interlayer distance should be greater than 1.5 nm [10] and the layered structure should be broken down [1]. The former occurs by ion exchange, replacing the original cations by more bulky organic ones, due to which the distance between the silicate layers is strongly enlarged, and the latter by high acting shear forces. The ion exchange is usually achieved with cationic surfactants such as alkylammonium or alkylphosphonium ions. As the modified clay becomes organophilic, its surface energy is lowered and it becomes more compatible with organic polymers. These polymers can then be intercalated within the galleries and this characteristic provides a way to prepare the rubber-clay nanocomposites. It was reported that the length of alkyl ammonium cations [11] and the presence of double bonds [12] are crucial factors for the preparation of exfoliated polymer clay nanocomposites. The polymer intercalation might be made more effective by increasing the interlayer distance. In this study two organoclays having different interlayer distance and modifying groups were used and their influence on the cure characteristics, mechanical properties and swelling behavior on natural rubber were investigated.

EXPERIMENTAL

Materials

Natural rubber of grade ISNR-5 was obtained from Rubber Research Institute of India, Kottayam, India. Two different types of nanoclay differing in the interlayer distance and in modifying groups were used for the study and were obtained from Southern Clay Products, USA. The interlayer distance of the clays used were 18.3 Å and 30.6 Å for cloisite 10 A [2MBHT: dimethylbenzylhydrogenatedtallow quaternary ammonium], and cloisite 15 A [2M2HT: dimethyldihydrogenatedtallow quaternary ammonium], respectively. Other chemicals used were of commercial grade.

Preparation of Natural Rubber-Clay Nanocomposites

Rubber compounds were prepared in a laboratory size (16 × 33 cm) two roll mill at a friction ratio of 1:1.25 as per ASTM D 3184 at room temperature. The compounding formulations used for study are given in Table 1. After mixing, the compound was homoganized by passing

TABLE 1 Compounding Formulation of the Rubber Compounds

Ingredients	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
Natural rubber	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Antioxidant-HS	1	1	1	1	1	1	1
Cloisite 10A	0	5	10	15	0	0	0
Cloisite 15A	0	0	0	0	5	10	15

six times through the tight nip of the mill and finally sheeted out. The compounds were kept overnight for maturation. Optimum cure time was determined using a Rubber Process analyzer (RPA 2000—Alpha Technologies). The compounds were vulcanized at a temperature of $150 \pm 2^{\circ}C$ and at a pressure of $200\,\mathrm{Kgcm^{-2}}$ in an electrically heated hydraulic press, to their respective cure times.

X-Ray Diffraction Studies

X-ray diffraction (XRD) technique was used to study the nature and extent of the dispersion of the clays in the rubber compounds. XRD patterns were collected using Bruker, D_8 Advance diffractometer at the wavelength $CuK\alpha = 1.54\,\text{Å}$, a tube voltage of 40 kV and tube current of 25 mA. Bragg's law, defined as $\lambda = 2d\sin\theta$, was used to compute the crystallographic spacing (d) for the clay. The samples were scanned in step mode by 1.0°/min scan rate in the range of $2\theta < 12^{\circ}$.

Measurement of Mechanical Properties

Tensile tests were performed on dumbbell shaped and tear tests on crescent shaped specimens punched out from the vulcanized sheets. The measurements were carried out at a crosshead speed of 500 mm per min on a Shimadzu Model AG1 Universal Testing Machine according to ASTM standards, D 412 and D 624, respectively.

Swelling Studies

Circular specimens of 0.2 cm diameter and 1 mm thickness were cut using a sharp-edged circular die from the vulcanized samples. The samples were immersed in about 15–20 ml of toluene contained in airtight bottles maintained at constant temperature. Samples were removed periodically and the surface adhered solvent drops were wiped off carefully by placing them between filter wraps. The weight of the swollen sample was determined immediately on a digital balance with an accuracy of +/− 0.001 mg. As the weighing was done within 30–40 s, the error due to evaporation of surface adsorbed solvent is considered insignificant.

Gas Permeability Testing

The air permeability of the natural rubber layered silicate membranes was measured using Lyssy Manometric Gas Permeability Tester L100-2402. The test gas used was oxygen at a rate of 500 ml/min. Permeability of the samples was calculated using the equation, $P_m = (T_r X P_r)/t_m$, where P_m is the permeability of the test sample, t_m is the interval time constant for the test sample, P_r is the permeability of the reference (standard PET sample), and T_r is the interval time constant for standard PET.

RESULTS AND DISCUSSION

Characterization of NR–Clay Nanocomposites Using X-Ray Diffraction Technique

Figure 1 shows the X-ray diffraction patterns of the cloisite 10A(a) and nanocomposite with 10 phr of clay loading (b). The cloisite 10 A clay

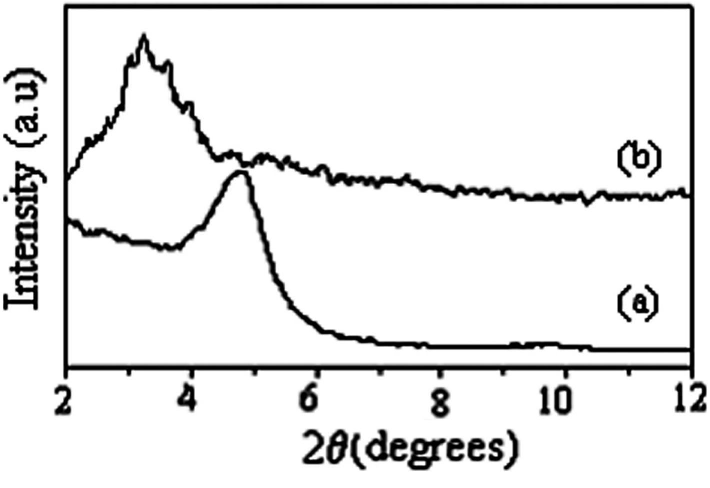

FIGURE 1 XRD patterns of cloisite 10 A (a) and NR-cloisite 10 A nanocomposite (b).

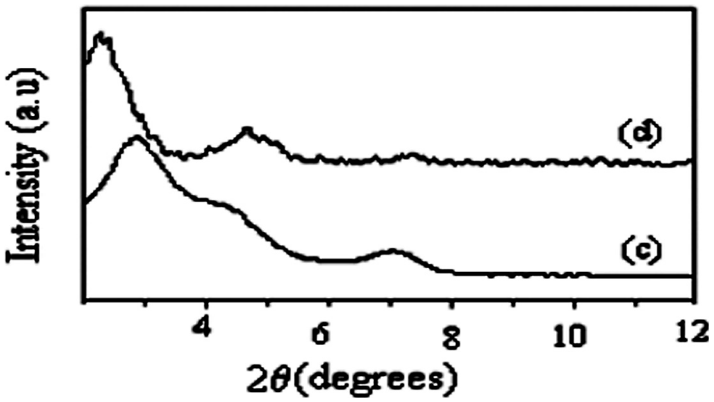

FIGURE 2 XRD patterns of cloisite 15 A (c) and NR-cloisite 15 A nanocomposite (d).

shows a diffraction peak at $2\theta = 4.80^\circ$ that is assigned to the interlayer platelet spacing (001 diffraction peak) of 18.39 Å. For 10 phr of clay-filled nanocomposites, the 2θ value shifts to a lower value, $2\theta = 3.16^\circ$ that is assigned to the interlayer spacing of 27.93 Å. Two more peaks at 24.66 Å and 22.07 Å, which are also higher than the interlayer distance of the clay, were observed. This increase in interlayer distance of the clay by approximately 9 Å confirms the formation of intercalated nanocomposite. Figure 2 depicts the XRD trace of cloisite 15A-NR nanocomposite, which possess two peaks at $2\theta = 2.23^\circ$ and 2.42° corresponds to the interlayer distance of 39.58 Å and 36.49 Å, respectively. These peaks are also displaced from the original 2θ value of cloisite 15 A, 2.88°, and interlayer distance 30.6Å. This increase in d spacing suggests the intercalation of the polymer chains between the clay layers.

Cure Characteristics of the Compound

The cure parameters derived from the rubber process analyzer is given in Table 2. The optimum cure time (t_{90}) was reduced in the presence of organoclays. It is reduced by almost three minutes for compounds containing 10 phr of nanoclay. This effect is attributed to the ammonium groups of the organic cations. In fact, amine groups facilitate the curing reaction of SBR and natural rubber stocks [1]. This reduction in cure time is slightly boosted with the increase in interlayer distance of the clay. The cure activation of organoclays is reported in the literature [13]. The intercalation of the organically modified clay within the silicate galleries facilitates the vulcanization reaction. A slight

TABLE 2 Cure Characteristics of Nanocomposites

Cure characteristics	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
Min Torque (dNm)	0.15	0.029	0.062	0.023	0.02	0.035	0.032
Max Torque (dNm)	2.229	3.115	3.117	3.154	3.52	3.736	4.354
T_{10} (minutes)	4.55	1.16	0.98	0.79	1.37	0.92	0.72
T_{50} (minutes)	6.07	2.6	2.47	2.21	2.69	2.42	2.24
T_{90} (minutes)	9.71	6.34	6.45	6.83	6.07	6.31	6.35

increase in cure time is observed as the clay loading is increased, this may be due to the adsorption of more curatives on the filler surfaces. A dramatic increase in maximum torque value with increase in clay content is also observed for the nanocomposites prepared using the two different clays (Figures 3 and 4). The maximum torque value gets doubled for the composite prepared with (10 phr) clay having higher interlayer distance. This increase in maximum torque value directs to the increase in modulus of the composites. These results are attributed to the intercalation of the polymer within the silicate galleries. Consequently a better interaction between the rubber and the filler

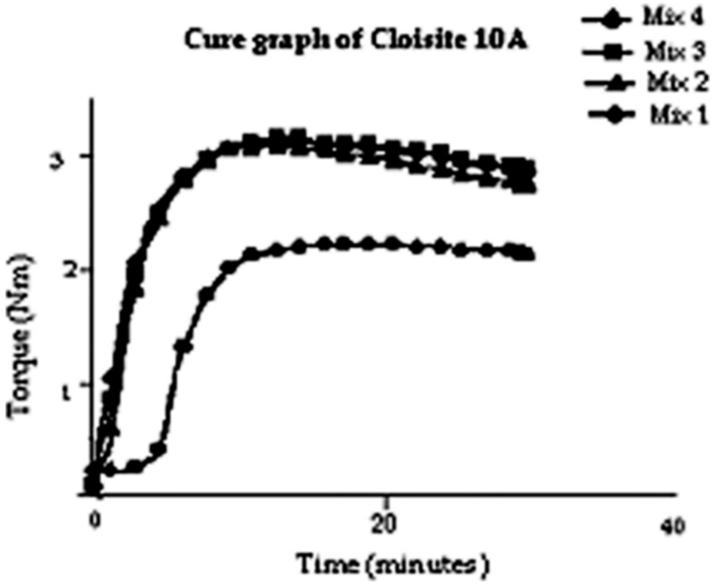

FIGURE 3 Typical cure graph of nanocomposite with cloisite 10A.

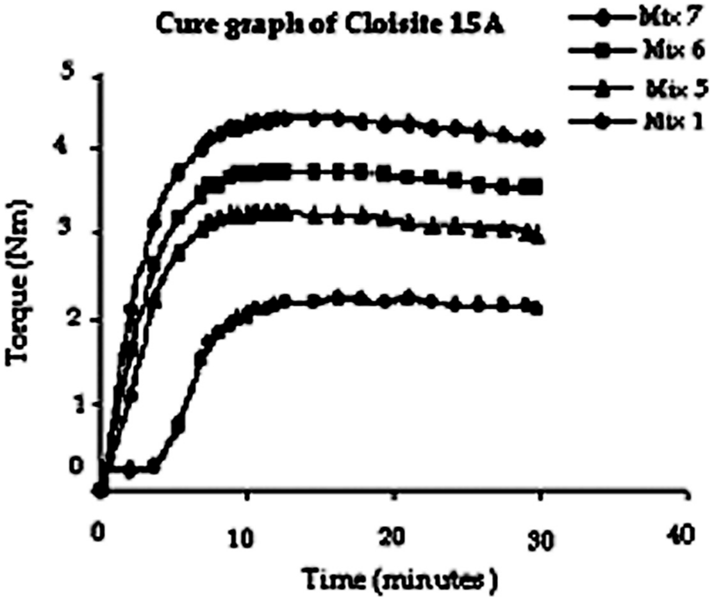

FIGURE 4 Typical cure graph of nanocomposite with cloisite 15A.

is obtained. The minimum torque values do not vary much with clay content suggesting the processability of the composites is not affected.

Mechanical Properties of Nanocomposites

The mechanical properties of the gum vulcanisate and nanocomposites are given in Table 3. The tensile properties measured are the modulus at different strains (100, 200, and 300% elongation), the tensile strength and elongation at break. A marked increase in mechanical properties is observed for the nanocomposites than the gum vulcanisate. The

TABLE 3 Mechanical Properties of the NR Mixes Containing Two Different Nanoclays

Physical properties	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
Tensile strength (MPa)	20.02	27.26	30.06	26.79	28.07	32.01	27.34
Elongation at break (%)	1231	992	950	932	918	891	839
Modulus at 100% elongation (MPa)	1.02	2.08	2.24	2.00	2.17	2.6	2.72
Modulus at 200% elongation (MPa)	1.22	2.52	2.93	2.72	2.78	3.4	3.48
Modulus at 300% elongation (MPa)	1.86	3.43	4.06	3.98	3.89	4.52	4.35
Tear strength (MPa)	38.02	39.00	42.27	40.86	45.3	52.5	42.92

mechanical properties increase with increase in clay content up to 10 phr. A further decrease is observed at higher clay loading, which may be due to the agglomeration of the clay. A 50% increase in tensile strength is obtained for the nanocomposite with 10 phr of clay (cloisite 15 A). Tear strength and modulus of the nanocomposites also shows the same trend. A 150% percentage increase in modulus at 300% elongation is obtained for the composite with cloisite 15 A. It is seen that the nanocomposite with the clay having higher interlayer distance shows the better mechanical properties. This suggests interlayer distance play a major role in the intercalation of the rubber matrix.

Swelling Studies

The mole percent uptake of the solvent by the nanocomposite is calculated from the diffusion data. The Q_t values were determined as

$$Q_t = \frac{(\text{Wt. of the solvent sorbed at a given time})/(\text{Mol wt. of the solvent})}{(\text{Initial wt. of the rubber specimen} \times 100)}$$

At equilibrium swelling Q_t becomes Q_∞. Sorption curves of the vulcanizate, obtained by plotting Q_t, mole% uptake per 100 g of the solvent against time are shown in Figure 5. For all compositions

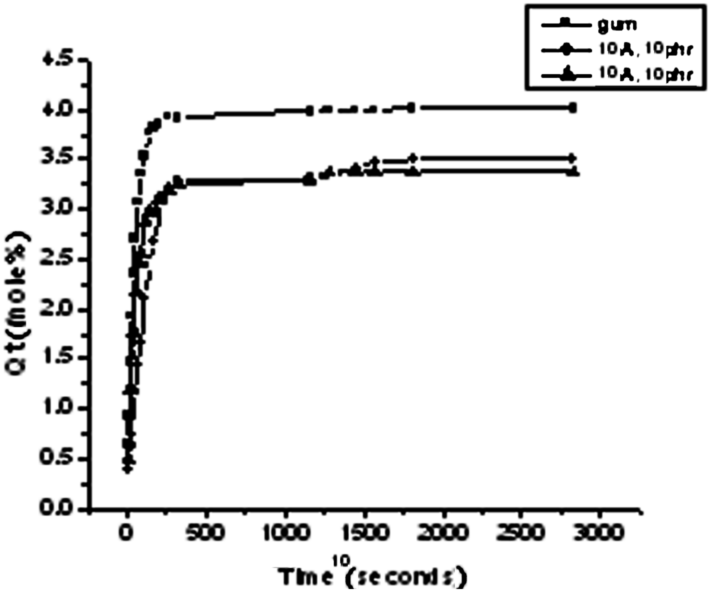

FIGURE 5 Sorption curves of natural rubber vulcanizates in toluene at 303 K.

the uptake is rapid in the initial zone. After this the sorption rate decreases leading to a plateau corresponding to equilibrium swelling. Note that the gum vulcanizate has maximum toluene uptake at equilibrium swelling and it is minimum for the composite with clay having higher interlayer distance. The swelling of the composite is strongly reduced in the presence of clay within the NR matrix. The molecular mobility is severely reduced in the close vicinities of the clay platelets and this, together with the obstruction of the clay itself provides a tortous path for the permeating molecules.

Gas Permeability Testing

The oxygen permeability of the gum and nanoclay filled vulcanizate of 2 mm thickness are given in Table 4. It is clearly seen that the oxygen permeability decreased substantially by incorporation of 5 phr of layered silicate. Higher permeation resistance is offered by the nanoclay having higher interlayer distance. This supports the better exfoliation, which resulted in the permeation resistance obtained by the incorporation of lower silicate loadings.

Gas barrier in polymer clay nanocomposites was traditionally explained in terms of Nielson model, originally adopted to describe the tortousity effect of plate-like particulates on gas permeability of filled polymer composite structures [14]. This model system consisting of uniform platelets homogeneously dispersed in the polymer matrix and oriented parallel to the polymer film surface. The model can be applied using the equation,

$$\frac{P}{P_0} = \frac{1 - \phi_f}{1 + (L/2W)\phi_f}$$

to obtain the clay aspect ratio from the permeability data of these nanocomposites. In the equation, P is the permeability of the nanocomposite, P_o is the permeability of the gum vulcanizate, and ϕ_f is

TABLE 4 Oxygen Permeability of the Rubber Vulcanizates and Aspect Ratio of Clay from Nielson's Model

Samples	Oxygen permeability (mL/m^2 day)	Aspect ratio from Nielson's model
Mix 1	824.19	
Mix 2	740.55	2.31
Mix 3	693.63	5.14

the volume fraction of the clay. L and W are length and width of the clay sheets, respectively, its ratio L/W, defines the aspect ratio α, of the fillers. The model assumes that the fillers are impermeable to the diffusing gas or liquid molecule, and are oriented formally to the diffusion direction. Aspect ratios calculated are given in Table 4. The samples with better dispersion present the highest aspect ratio as suggested by the permeability data. Thus, the presence of the filler particles creates tortous path for the permeant to travel through the composites.

CONCLUSION

Natural rubber–organoclay nanocomposites were prepared with two different types of nanoclay in varying clay loading and their properties were compared. For the two nanocomposites formed the optimum amount of clay loading was found to be 10 phr and then a decrease in properties, which may be due to the agglomeration of clay particles, was observed. The vulcanization rate and torque value of the nanocomposites were found to be sensibly higher than the gum compound. Both solvent and gas permeation resistance of the nanocomposites is evident from the results obtained. The presence of a tortous path for the permeating molecules is confirmed by the Nielson's model. It was found that the nanocomposite with clay having higher interlayer distance posses better properties. As the interlayer distance increases, polymer chains could penetrate more easily into the clay layers, which results in the formation of an intercalated structure. The decrease in d spacing for these layered clays evident from X-ray results also confirmed the formation of an intercalated structure.

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