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J. Rubb. Res., **8(1)**, 1–15

REPRINT

Natural Rubber Latex-based Nanocomposites with Layered Silicates

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Sulphur prevulcanised natural rubber latex (PVNRL) nanocomposite was produced by mixing dispersions of layered silicates with prevulcanised latex. In this study layered silicates such as bentonite (natural) and fluorohectorite (synthetic) were used in addition to a non-layered amorphous filler (English Indian clay) as reference material. After compounding the layered silicate dispersions with PVNRL, films were prepared by casting. The vulcanised films of PVNRL nanocomposites were subjected to mechanical, swelling, X-ray diffraction and transmission electron microscopic studies. In all respects, layered silicate nanocomposites registered superior properties compared to the reference material. This was explained to be due to the intercalation/exfoliation of the silicate layers by natural rubber. It was found that the fine silicate layers formed a skeleton network structure (house of cards) in the vulcanisate.

Key words: layered silicates; nanocomposites; natural rubber; latex; prevulcanisation; sulphur; bentonite; fluorohectorite; clay

Vulcanised rubbers are usually reinforced by carbon black and also by inorganic minerals (clay, calcium carbonate, silicates *etc.*) to improve the mechanical properties. Carbon black offers excellent reinforcement owing to its strong interaction with rubbers, but its presence especially at high loading, often decreases the processability of rubber compounds. The reinforcing capacity of silicates is poor because of their large particle size and low surface activity. Nowadays there is great interest in the development of polymeric nanocomposites using layered silicates as reinforcing material[1–6]. Provided that the layered silicates fully delaminate (termed exfoliation) dispersing less than 10% of them, may replace 3-4 times higher amount of traditional fillers without sacrificing the processability and mechanical properties. Though the concept of nano-reinforcement with layered silicates, credited to researchers at Toyota Central Research Laboratories (Japan), it became very popular in late 1980s, which has been well reviewed[6–7]. Polymer nanocomposites represent a new alternative to conventionally (macroscopically) filled polymers. Because of their nanometre scale filler dispersion, nanocomposites exhibit markedly improved properties when compared to pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties,

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improved solvent and heat resistance and decreased flammability[7–10].

Nanocomposite preparation includes *in situ* polymerisation, solution and melt intercalation. A powerful approach to produce layered silicate polymer nanocomposites is melt intercalation of polymers. This is a common method and is generally applicable to a range of plastics from essentially non-polar through weakly polar to strongly polar polymers. Layered silicate polymer nanocomposites are processable using latest technologies. In general two types of organic/inorganic hybrids are distinguished: intercalated (polymer chains are diffused between the silicate layers preserving, however, some short range order of the latter) and dispersed (in which the silicate layers of *ca.* 1 nm thick are exfoliated and dispersed in the polymer matrix). Pristine layered silicates usually contain hydrated Na+ or K+ ions. Ion exchange reactions with cationic surfactants, including ammonium ions render the normally hydrophilic silicate surface organophilic. This is the prerequisite for intercalation with many engineering polymers. The role of the alkyl ammonium cations in the 'usual' organosilicates is to lower the surface energy of the silicate and to improve its wettability by the polymer. Additionally, the alkyl ammonium compounds may contain functional groups, which can react with the polymer or initiate the polymerisation of monomers. This may strongly improve the strength of the interface between the silicate and the polymer[11–12].

Minerals have a variety of shapes suitable for reinforcement of polymers, such as fibrils and platelets. Layered silicate is comprised of platelets having a planar structure of 1 nm thick and 200 nm–300 nm length. The layers cannot be separated from each other through general rubber processing. Since inorganic ions absorbed by silicates can be exchanged with organic ions, efforts in intercalating many kinds of polymers and to prepare clay/polymer nanocomposites have been reported[13–17]. It has been shown that the silicate layers can be dispersed at molecular level (nano-metre scale) in a polymer matrix[8]. Modulus enhancement is essential for certain latex products like catheters, surgical tubing *etc.* Rubber-clay nanocomposites were prepared from latex by a coagulation method and an improvement in mechanical properties was reported[14–15]. Some layered silicates are suitable additives for latex, provided that they can form dispersions adequate for latex compounding[16]. In aqueous dispersions, the clay 'swells' (*i.e.* its layers are separated by hydration) which makes the intercalation due to rubber molecules possible. In this study natural rubber (NR) latex in the prevulcanised form was used to prepare nano-composites. Properties of the nano-composites were compared with vulcanisates containing an inert filler called English Indian clay (commercial, non-layered silicate).

EXPERIMENTAL

Materials

Details of the silicates used are given in *Tables 1 A* and *1 B*. Sodium fluorohectorite (Somasif ME-100®) of Coop Chemicals, Japan is a synthetic layered silicate whereas sodium bentonite (EXM 757®) of Sud Chemie, Germany is a purified natural layered silicate. Details of the commercial clay (English Indian Clays, India) used are given in *Table 1 B*. The formulation used for preparing prevulcanised latex is given in *Table 2*. Centrifuged NR latex — high ammonia (HA) type—with 60% dry rubber content, conforming to *Bureau of Indian Standards (BIS)* specification 5430, (*Table 3*) was supplied by the Rubber Research Institute

TABLE 1A. DETAILS OF THE LAYERED SILICATES

Trade name	Chemical name	Chemical formula	Ion exchange capacity (meq/100g)	Layer distance (nm)
Somasif ME-100®	Na-fluorohectorite	$(Mg_{5.2}\ Li_{0.8})\ (Si_8)O_{20}\ (OH)_{4-x}\ (F)_x\ Na_{0.8}$	100	0.94
EXM 757®	Na-bentonite	$(Al_{3.2}\ Mg_{0.8})\ Si_8O_{20}\ (OH)_4\ Na_{0.8}$	80	1.24

TABLE 1B. DETAILS OF THE ENGLISH INDIAN CLAY

English India Clay	Contents (mass %)
SiO_2	45
Al_2O_3	38
Fe_2O_3 (max)	0.5
TiO_2	0.55
CaO (max)	0.06
MgO (max)	0.07
Na_2O (max)	0.25
K_2O (max)	0.10
Loss of ignition	15.47

TABLE 2. FORMULATION OF PREVULCANISED LATEX

Ingredients	Dry	Wet
60% Natural rubber latex	100	167.0
10% KOH solution	0.25	2.5
10% Potassium oleate	0.16	1.6
50% Sulphur dispersion	1.25	2.5
50%[a] ZDC dispersion	0.80	1.6
50% ZnO dispersion	0.25	0.5

[a] Minimum
ZDC: Zinc diethyldithiocarbamate

TABLE 3. SPECIFICATIONS OF CONCENTRATED LATEX (W/W, %) – *BIS 5430-1981*

Properties	Value	Requirements (*BIS 5430-1981*)
Dry rubber content	60	60[a]
Non-rubber solids	1.5	2[b]
Sludge content by mass	0.5	0.1[b]
Ammonia content by mass	0.8	0.6[a]
Potassium hydroxide number	0.5	1[b]
Mechanical stability time (sec)	1000	475[a]
Volatile fatty acid number	0.02	0.15[b]
Coagulum content by mass	0.03	0.05[b]
Copper content (p.p.m.)	1	8[b]
Manganese content (p.p.m.)	Traces	8[b]

[a]Minimum; [b]Maximum

of India. Sulphur, zinc diethyldithiocarbomate and zinc oxide were supplied by Bayer, Germany and used as aqueous dispersions. Aqueous dispersions (10%) of layered silicates were prepared in a ball mill.

Prevulcanization of Latex

For prevulcanisation the concentrated high ammonia (1%) latex having 60% dry rubber was mixed with the ingredients listed in *Table 2* under slow stirring for 4 h in a circulating water bath. The temperature of latex was maintained at 55 ± 1°C. Loss of ammonia was compensated for adding freshly prepared ammonia solution (1%). The prevulcanised latex (chloroform number 2) thus obtained was cooled to room temperature and kept in sealed plastic containers.

Film Casting

The prevulcanised latex was mixed with aqueous dispersions of silicates at different loadings, after removing the dirt and coarse particles by filtering through a sieve (opening: 250 micron). It was then cast on raised glass plates having dimensions of 13 cm × 10 cm × 2 mm. The casting was allowed to dry at room temperature until transparent and further vulcanised at 70°C for 2 h in an air-circulated oven. The post-vulcanisation was carried out to ensure maximum mechanical properties to the film. The samples thus obtained were kept in a desiccator for mechanical testing.

Testing

Tensile tests were performed on dumb-bell shaped specimens according to the *ASTM D-412* on a Zwick 1485 universal testing machine at a crosshead speed of 50 cm per minute. Tear strength was conducted using crescent shaped samples according to *ASTM D 624-00*.

X-ray diffractograms (XRD) were obtained by a D500 diffractometer (Siemens, München, Germany) using Ni-filtered CuK_{α} radiation

($\lambda = 0.1542$ nm). The samples were scanned in step mode by 1.5°/min scan rate in the range of $2\theta < 12°$. Transmission electron microscopic (TEM) studies were carried out with a LEO 912 Omega transmission electron microscope (Carl Zeiss, Oberkochen, Germany) with an acceleration voltage of 120 keV. The specimens were prepared using an Ultracut E ultramicrotome (Leica Microsystems, Wetzlar, Germany) equipped with a cryochamber. Thin sections of about 100 nm were cut with a diamond knife at –120°C.

The stress relaxation was carried out on samples elongated to 500% at a strain rate of 25 mm/min. The relaxed stress was calculated by dividing the stress after 10 min by the initial stress (σ_{10}/σ_0). Tension set was measured using dumb bell shaped sample stretched to a particular elongation (5 times) for 15 minutes and thereafter the permanent set was noted. For swelling studies the circular specimens of 1.98 cm diameter were cut using a sharp edged circular die. The initial weight was taken and the samples were immersed in toluene bottles and kept at constant temperature (25°C) for 48 h. The samples were removed from the test bottles, adhering solvent was blotted off the surface, and the samples weighed in airtight bottles on a sensitive electronic balance. The quantity of solvent absorbed was expressed as weight in grams of solvent absorbed per 1g of the composite (swell index). V_r, values of samples were calculated using the Ellis and Welding equation[18]:

$$V_r = \frac{(D\text{-}FT)\ \rho r^{-1}}{(D\text{-}FT)\ \rho r^{-1} + A_0\ \rho_s^{-1}} \quad \dots 1$$

D is the de-swollen weight, F is the weight fraction of filler, A_0 is the solvent absorbed, T is the sample weight, ρr — specific gravity of rubber (0.92), ρ_s — specific gravity (0.86) of solvent[19].

RESULTS AND DISCUSSION

XRD Studies

The XRD spectrum of the layered silicates showing the interlayer distances is given in *Figure 1*. The interlayer distance can be calculated from the Bragg's equation $n\lambda = 2d \sin\theta$ where n is the order of diffraction, d is the interlayer distance and λ is the wavelength of X-ray (0.1542 nm) and θ is the angle of diffraction[20]. Lower the value of 'θ', grater will be the interlayer distance. The XRD spectrum of fluorohectorite showed 3 peaks, which from left correspond to interlayer distances of 1.35, 1.24 and 0.96 nm, respectively. The strong peak at 0.96 nm showed that majority of the layers in fluorohectorite has an interlayer distance of 0.96 nm. The bentonite showed one peak, which corresponds to an interlayer distance of 1.24 nm. The commercial clay has one small peak at 0.72 nm, which is not at all ideal for polymer intercalation as the interlayer distance is too small[1].

TEM Studies

It will be interesting now to analyse the TEM pictures of the composites. All the composites are loaded with 10 p.h.r. of filler. In *Figure 2a*, the TEM of commercial clay (English Indian clay) loaded vulcanisate is given. Here the filler exists as large particles and the filler distribution is not homegeneous. This means, 10 p.h.r. loading of the commercial clay is not enough to saturate the polymer phase as they exist as big particles distributed unevenly which in effect weaken the matrix. It is pertinent that this clay was not a layered version. However, in bentonite filled vulcanisate (*Figure 2b*), the filler exists as a network of fine silicate layers around the rubber particles (white portion). This is

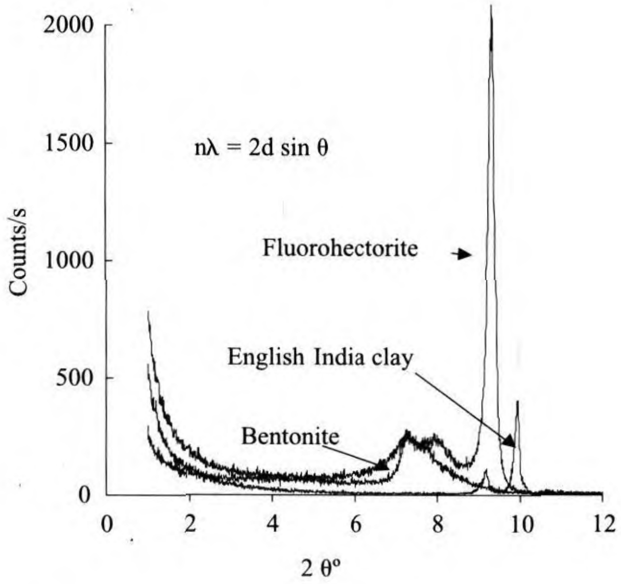

Figure 1. Wide angle X-ray diffraction pattern of layered (bentonite and fluorohectorite) and the non-layered silicate (English Indian clay).

because the bentonite clay underwent some level of intercalation with rubber hydrocarbon, and the silicate layers form 'clusters or house-of-cards structure'[1,16]. The high compound viscosity, which has been experienced during mixing, might be due to the formation of the layer network structure. The polymer phase is reinforced to a great extent as it is saturated with this network structure which, in turn, contributed to the greater mechanical properties to the vulcanisate. However, a fully homogeneous structure was observed in fluorohectorite-filled vulcanisate (*Figure 2c*). Here, the silicate layers were intercalated to a greater extent[16] and a small level of exfoliation was also observed which exists as thin black strands in the photograph. Some level of network structure and orientation were also visible here which may be responsible for the higher modulus of fluorohectorite filled vulcanisate compared to that of bentonite. Moreover, the exfoliated structure gives a several-fold increase in surface area.

Mechanical Properties

Figures 3a, *3b* and *3c* show the modulus at various elongations for different silicate-filled vulcanisates. *Figure 3a* illustrates the results of 3 p.h.r. loaded vulcanisate. It is to be noted that at low elongation (100%) there is a gradual increase in modulus, which is in the order, gum< English Indian clay < bentonite < fluorohectorite. It is to be noted that the superior increase in modulus is with fluorohectorite at 300% elongation followed by bentonite. *Figure 3b* represents the modulus change with various silicates at 5 p.h.r. loading. Here also the change in modulus at various

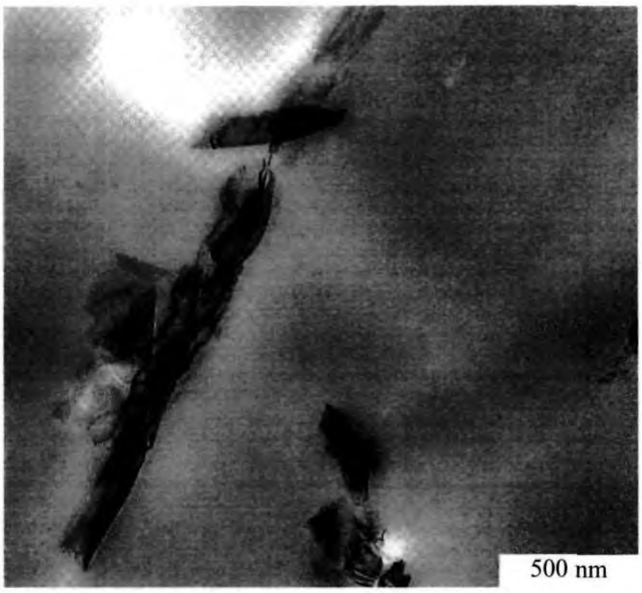

Figure 2a. Transmission Electron Micrographs of 10 p.h.r. English Indian clay loaded NR latex vulcanisate.

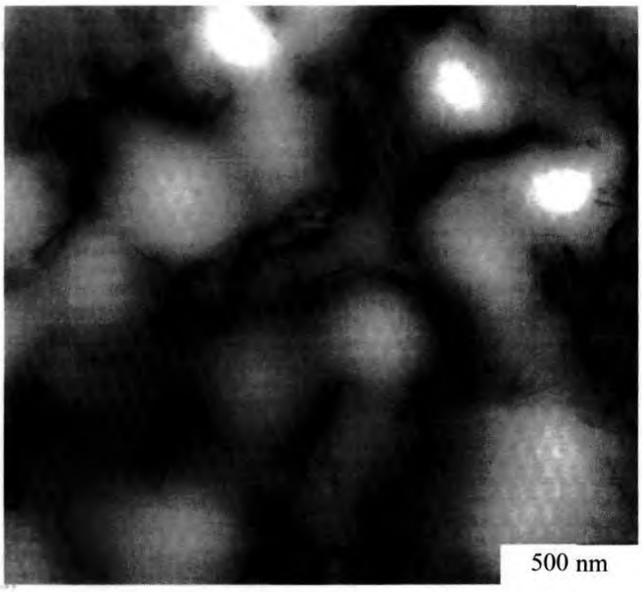

Figure 2b. Transmission Electron Micrographs of 10 p.h.r. bentonite loaded NR latex nanocomposites.

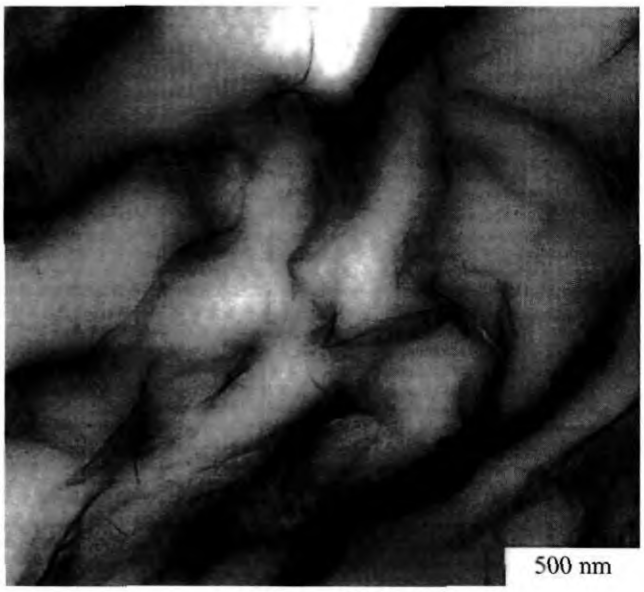

Figure 2c. Transmission Electron Micrographs of 10 p.h.r. fluorohectorite loaded NR latex nanocomposites.

elongations is of the same order as we have discussed earlier. However, at the same elongation the magnitude of the modulus at 5 p.h.r. loading is higher when compared to that at 3 p.h.r. loading (*Figure 3a*) especially with layered silicates. In the case of commercial clay-filled vulcanisates this difference is negligible. The silicate layers may favour the formation of immobilised or partially immobilised polymer phases, which may contribute for high modulus[21]. Moreover, the sheets of layered silicates orient along the strain direction, which increases with increased strain. The low stiffening effect of commercial clay can be attributed to its high particle size and poor dispersion. In the vulcanisate containing layered silicate, a part of the silicate was exfoliated which offers high surface area for reinforcement. When the loading is increased to 10 p.h.r. (*Figure 3c*), layered silicates showed comparatively high modulus.

The effect of filler loading on tensile strength of the composites is shown in *Figure 4*, which was found to increase up to 5 p.h.r. loading of layered silicates and thereafter it decreases. This might be due to the agglomeration of the fine silicate layers beyond a particular concentration in the polymer. In the case of layered silicates the critical concentration was found to be 5 p.h.r. The increase in tensile strength is not as expected for nanocomposite. This might be due to the high molecular size of the prevulcanised rubber latex, which may hinder the intercalation process[16].

Tear strength values of the composite are given in *Table 4*. Addition of a small amount of

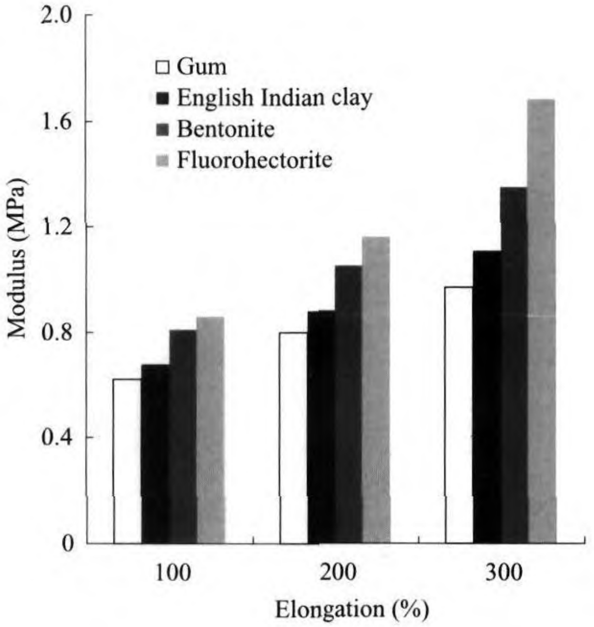

Figure 3a. Moduli at different elongations for different silicates-filled (nano) composites at a loading of 3 p.h.r.

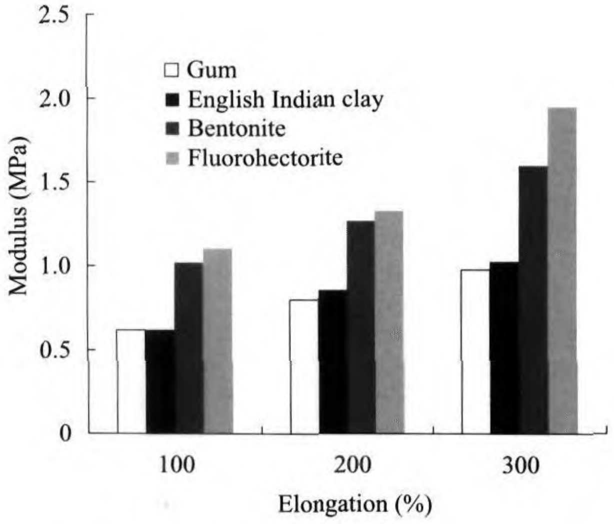

Figure 3b. Moduli at different elongations for different silicates-filled (nano) composites at a loading of 5 p.h.r.

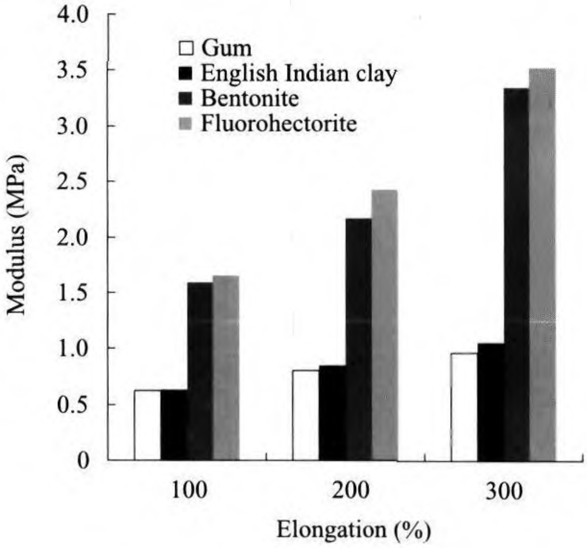

Figure 3c. Moduli at different elongations for different silicates-filled (nano) composites at a loading of 10 p.h.r.

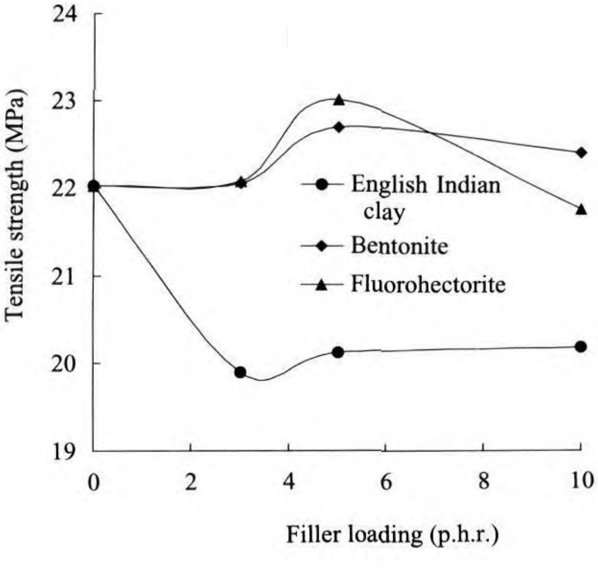

Figure 4. Tensile strength of different silicates-filled (nano) composites at different loading.

TABLE 4. TEAR STRENGTH OF LAYERED SILICATE-FILLED (10 P.H.R.) VULCANISATES

Silicate	Loading (p.h.r.)			
	0 (Control)	3	5	10
Fluorohectorite (kN/m)	47.9	60.5	58.2	28.8
Bentonite (kN/m)	47.9	51.4	48.9	23.2
English Indian clay (kN/m)	47.9	41.1	48.8	41.8

layered silicate (3 p.h.r.) increased the tear strength considerably. It has been reported that exfoliated layered silicates can increase the tear strength considerably[21]. However, as the amount of silicates increased, the tear strength decreased whereas for English Indian clay, addition of filler decreased the tear strength irrespective of the amount of loading. From this it can be concluded that exfoliated silicate layers hinder/divert the tear path[16,22] which results in high tear strength value in fluorohectorite and bentonite. At high loading (above 5 p.h.r.) the silicate layers may agglomerate and exist as stacks. That may be the reason for the low tear strength values of 10 p.h.r. loaded samples. In the case of tear strength, the threshold level of silicate (layered) loading was observed to be 3 p.h.r.

The rate of relaxation of the composites with stress was fast in the case of layered silicate (*Figure 5*) incorporated vulcanisates and it is in the order, fluorohectorite > bentonite > English Indian clay. At high elongation the chain slip along the filler surface is the major factor, which contribute to the stress decay, which is proportional to the surface area of the filler in contact with the polymer. As the extent of exfoliation is high in fluorohectorite, the surface area and hence the stress decay at a given elongation is proportionately higher in fluorohectorite.

Tension set of the composites was determined and is given in *Table 5*. Set was greatest with fluorohectorite, which is typical for reinforcing fillers. The results showed that as the loadings of layered silicate increased the set also increased. The tension set increase in the order, English Indian clay < bentonite < fluorohectorite.

Swelling Behaviour

Table 6 shows the weight in grams of toluene absorbed per gram of the composite at 25°C. The gum vulcanisate has the greatest toluene uptake at equilibrium swelling. This was expected, since there was less restriction for the solvent absorption through the vulcanisate. At equal volume loading of filler, the amount of solvent absorbed at equilibrium swelling is less for the composites containing layered silicate — especially with fluorohectorite — compared to that containing commercial clay. The presence of impermeable clay layers decreases the migration by increasing the average diffusion path length in the specimen[22-23]. In commercial clay-filled rubber, the solvent uptake is greater because of the weak interface and also due to poor clay dispersion. In well-oriented composites, the penetration perpendicular to the orientation is highly restricted.

The Kraus plots of the vulcanisates are given in *Figure 6*. It is the ratio of the volume fraction of rubber in the unfilled material to that of the filled vulcanisate ($V_r o/V_r f$) against volume fraction of filler (ϕ). If the value

TABLE 5. TENSION SET (%) OF LAYERED SILICATE-FILLED VULCANISATES

Silicate	Loading (p.h.r.)			
	0 (Control)	3	5	10
Fluorohectorite	2	10	16	36
Bentonite	2	8	14	18
English Indian clay	2	2	6	10

TABLE 6. SWELLING BEHAVIOUR—AMOUNT OF TOLUENE ABSORBED PER GRAM OF THE VULCANISATE CONTAINING SILICATES AT 25°C

Silicate	Loading (p.h.r.)			
	0 (Control)	3	5	10
Fluorohectorite	4.93	4.74	4.49	4.31
Bentonite	4.93	4.85	4.60	4.35
English Indian clay	4.93	4.89	4.83	4.73

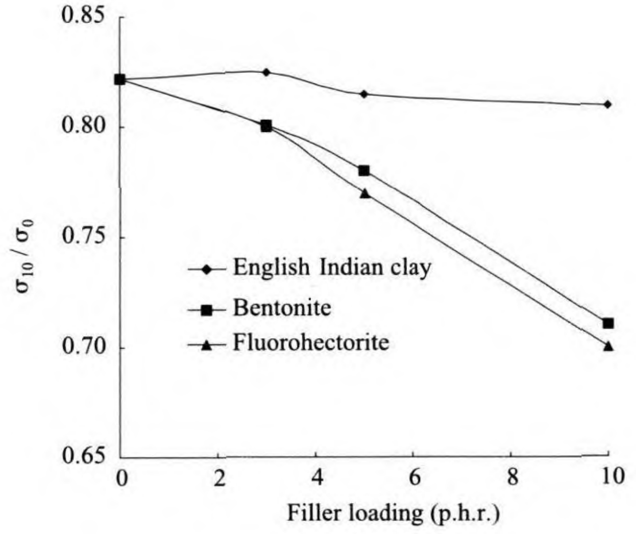

Figure 5. Relaxation of stress after 10 min for different silicate-filled (nano) composites.

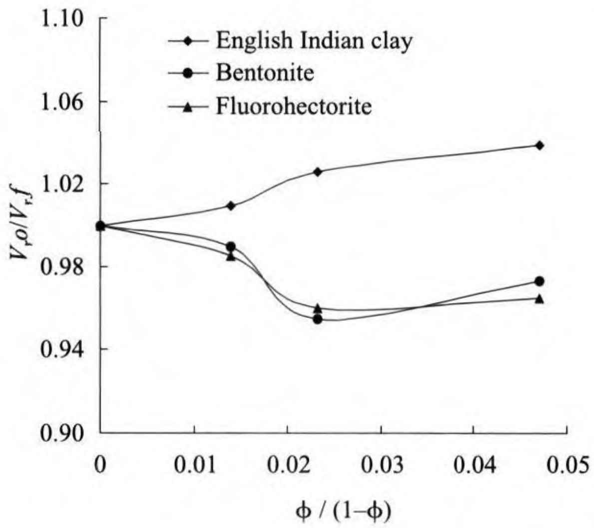

Figure 6. Plots of $V_r o/V_r f$ *against volume fraction of filler for different silicates-filled (nano) composites.*

$V_r o/V_r f$ is less than unity the filler rubber interactions are more and *vice versa*. It is interesting to note that for the layered silicates $V_r o/V_r f$ is less than one and the magnitude of the ratio decreases with filler loading. However, in the case of English Indian clay the $V_r o/V_r f$ is always higher than 1. Hence, these composites showed low reinforcement and poor mechanical properties.

CONCLUSIONS

Nanocomposites based on sulphur prevulcanised natural rubber latex and layered silicates were prepared. The vulcanised nanocomposite was subjected to mechanical and TEM analysis. It was found that the modulus and tear strength of the vulcanisate increased with the incorporation of layered silicate and in the case of layered silicates, 3 p.h.r. loading was found to be the threshold level for most of the mechanical properties. Higher loading led to agglomeration of filler in the rubber. It was also found that the rate of relaxation of stress and tension set were higher for layered silicate incorporated materials. The solvent resistance of the material was better compared to the reference. The filler-rubber interactions are strong in layered silicate-incorporated vulcanisate as evident from plots.

Date of receipt: June 2004
Date of acceptance: April 2005

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