Natural Rubber Latex Nanocomposites

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Abstract: Natural rubber (NR) based nanocomposites with 10 wt % natural and synthetic layered silicates were produced via the latex compounding method. As layered silicates, sodium bentonite (natural) and sodium fluorohectorite (synthetic) were selected in addition to a non-layered inert filler (English India Clay or commercial clay) as reference material. The nanocomposites were prepared by compounding the dispersions of clays and other latex chemicals necessary for vulcanization. The vulcanized nanocomposites were subjected to mechanical, thermal and swelling tests. The silicate dispersion was studied by transmission electron microscopy (TEM). Layered silicates outperformed the reference material (commercial clay) in all aspects. This was attributed to the intercalation/exfoliation of the silicates and to the formation of a skeleton "(house of cards)" silicate network in the NR matrix.

1. Introduction

Polymer nanocomposites represent a new alternative to conventionally (macroscopically) filled polymers. Because of their nanometer size filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability [1-3]. This nano-concept is highly relevant for rubber compounds since their application requires filler reinforcement [4-8].

Here the conventional compounding technique was used to prepare nanocomposites from latex. Layered silicates are suitable additives for latex, provided that they can form dispersions adequate for latex compounding. In aqueous dispersions, the clay "swells" (i.e. its layers are separated by hydration) which makes its good dispersion possible. In this study NR latex was compounded with dispersions of layered silicates and other vulcanizing ingredients in order to produce vulcanized natural rubber-clay nanocomposites. Properties of the nanocomposites were compared with vulcanizates containing an inert filler (commercial, non-layered clay) used in many latex products to make them cheap.

2. Experimental

Sodium fluorohectorite (Somasif ME-100) of Coop Chemicals, Japan is a synthetic clay, which has an ion exchange capacity of 100 meq/100g and an inter-layer distance of 0.94 nm. Sodium bentonite (EXM 757) of Süd Chemie, Germany is a purified natural clay, having an ion exchange capacity and interlayer distance 80 meq/100g and 1.24 nm, respectively. Commercial clay (English India Clays, India) was a mixture of oxides of Si, Al and Fe. The base formulation for preparing NR nanocomposites from latex is given in Table 1. Centrifuged NR latex - high ammonia (HA) type- with 60% dry rubber content, conformed to BIS specification 5430, was supplied by Rubber Research Institute of India. Sulphur, zinc diethyl dithiocarbomate, zinc oxide and styrenated phenol (SP) were supplied by Bayer, Germany and used as their aqueous dispersions. The latex was mixed with the compounding ingredients according to the formulation given in Table 2 and stirred well for

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half an hour for a homogeneous mixture. Vulcanized latex films were prepared by dry-casting and subsequent heating at 100 °C for 1 hour.

Tensile tests were performed on dumb-bell shaped specimens on a Zwick 1485 universal testing machine at a crosshead speed of 50 cm per minute. The dynamic-mechanical thermal analysis (DMTA) spectra were taken on rectangular specimens (6x 1x 0.25 cm^3) in tensile mode at a frequency of 10 Hz using a Eplexor 150 N device of Gabo Qualimeter, Germany, at a heating rate of 2 °C /min. Thermogravimetric analysis was done using a Thermal Analyser (Mettler Toledo TC-15, Germany) in the temperature range of 30 - 600 °C. Transmission electron microscopic (TEM) studies were carried out with a LEO 912 Omega transmission electron microscope with an acceleration voltage of 120 keV.

Table1. Base formulation

Ingredients	Wet	Dry
	(Parts by weight)	
60% Natural rubber latex	167.0	100.0
50% [a] ZDC dispersion	2.0	1.0
50% Clay dispersion	20.0	10.0
50% Sulphur dispersion	3.0	1.5
50% [b]AO SP dispersion	2.0	1.0
5% Zinc oxide	3.6	1.8

a- Zinc diethyl dithiocarbomate (ZDC)
b-Antioxidant(AO); styrenated phenol (SP)

3. Results and Discussion

3.1. Mechanical properties

The stress-strain curves of the vulcanizates are illustrated in Figure 1. Here also, the load at all elongations is highest for the fluorohectorite. It is worth of noting that the strain-induced crystallization of NR is not at all affected, as it is evident from the strong increase in stress after 500 % elongation. The initial high stress is due to the reinforcement of the rubber by the clay layers. However as elongation increases, (> 400 %) stress induced crystallization comes in to role, which increases proportionally with elongation. It is to be noted that at the breaking point the curves come together except the compound with fluorohectorite.

The nanometric dispersion of silicate layers means an efficient reinforcement, which leads to improved stiffness. The silicate layers may favour the formation of immobilized or partially immobilized polymer phases, which also increases the stiffness [1]. It is also possible that the orientation of silicate layer is responsible for the observed reinforcing effect. The low stiffening effect by commercial clay can be attributed to its high particle size and poor dispersion in the matrix.

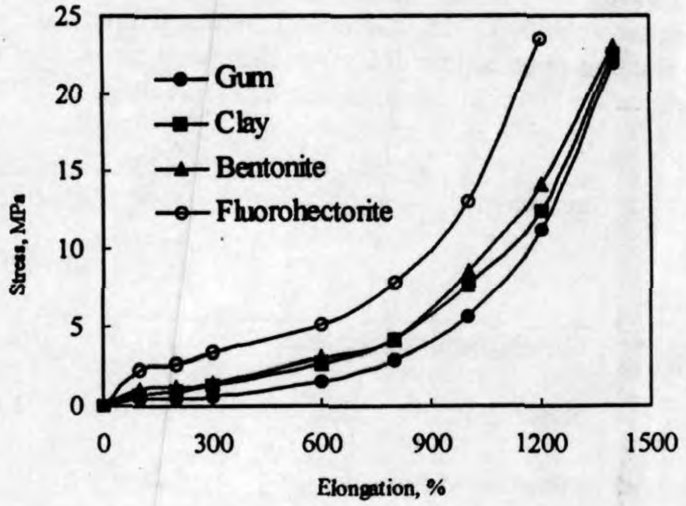


Figure 1. Stress-strain curves for the clay filled (nano)composites.

Figures 2a to 2b depict the dynamic mechanical spectra (dynamic storage modulus E′ and loss factor tan δ) as a function of temperature for the composites. There is a remarkable increase in the storage modulus for both layered silicate filled composites compared to the commercial clay. The storage modulus below the glass transition temperature (Tg = - 70°C) is increased by 400 % for fluorohectorite and 450 % for bentonite when compared to commercial clay filled polymer. In Figure 2b the loss factor tan δ is shown for different clay filled vulcanizates. Unlike other vulcanizates, the tan δ curve of fluorohectorite showed a broad relaxation process from ambient temperature to 100 °C.

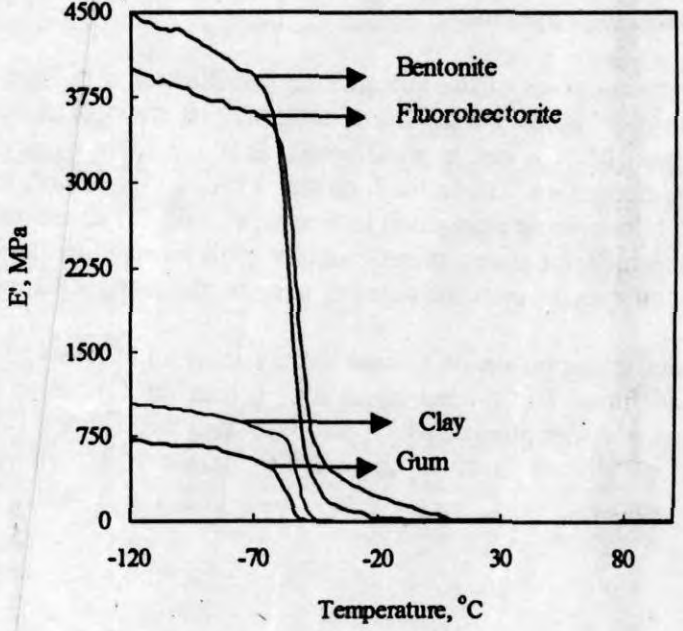


Figure 2a. Storage modulus (E') as a function of temperature.

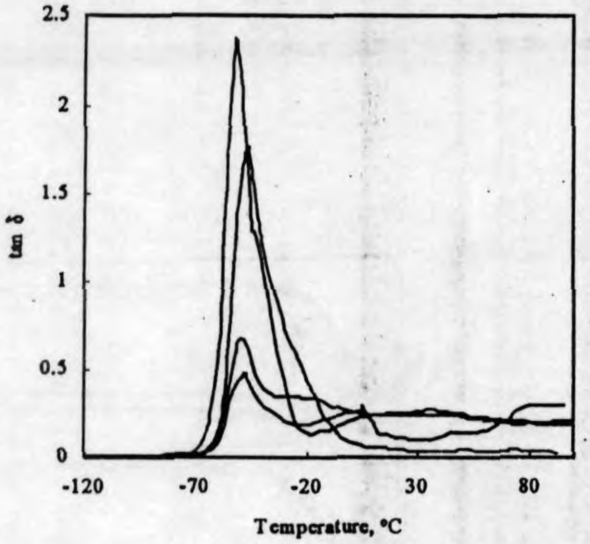


Figure 2b. Mechanical loss factor (tan δ) against temperature for clay filled (nano) composites.

This may be due to the sliding of the intercalated silicate layers expanded by interstitial rubber [4] or may represent the relaxation of rubber fraction confined inside the layers. It is noteworthy that in the case of commercial clay filled composites, which have no interstitial (confined) rubber, no such portion in the tan δ curve can be seen.

The maximum of tan δ peak reduces significantly suggesting a strong adhesion between NR and silicate. Sliding along the intercalated interlayer is suppressed. In addition, chain slipping at the outer surfaces of the aggregates is likely also hampered. Therefore the loss maximum is smallest in case of the system with the strongest filler matrix coupling (fluorohectorite).

3.2. Thermal decomposition

At 400 °C, the percentage of weight retained is higher for the nanocomposites (data not shown). This increase in thermal stability of the hybrid may result from the dispersion of the clay and from a strong interaction between the clay platelets and rubber molecules. At 450 °C, fluorohectorite filled vulcanizate is more stable than the bentonite filled version. This is a hint for the dispersion state of the layered silicates in the rubber. It has been reported that hybrids with a good dispersion of organoclay are thermally more stable. A characteristic feature of the nanocomposites is that the thermal property improvement occurs at very low filler content, often making the obtained material cheaper, lighter and easier to process than conventional composites.

3.3 Sorption behaviour

Figure 3 shows the sorption curves of the vulcanizates, which are obtained by plotting Q_t (mole per cent uptake per 100g of the composite) in toluene at 25 ^{0}C. Note that the gum has the maximum toluene uptake at equilibrium swelling. This is expected, since there is less restriction for the penetrant to diffuse into the vulcanizate. At equal volume loading of filler, the amount of solvent absorbed at equilibrium swelling is less for the composites containing layered silicate - especially fluorohectorite - compared to that containing commercial clay.

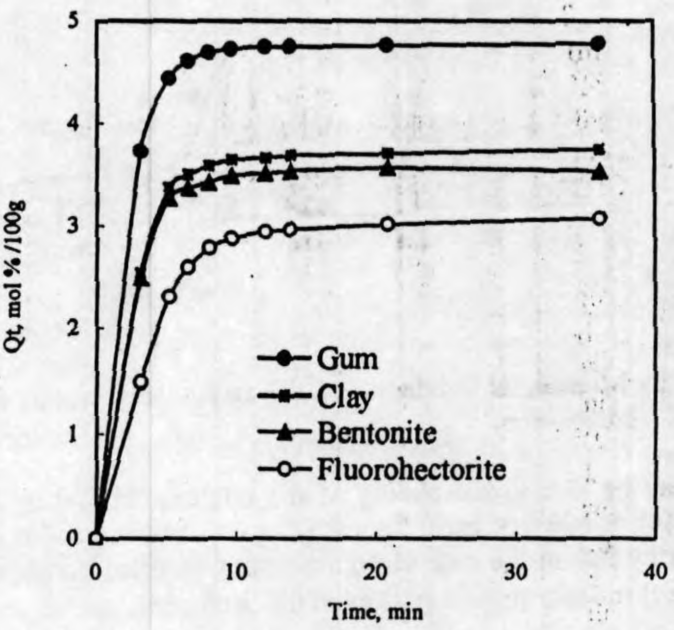


Figure 3. Swelling behaviour of the clay filled (nano)composites in toluene at 25°C.

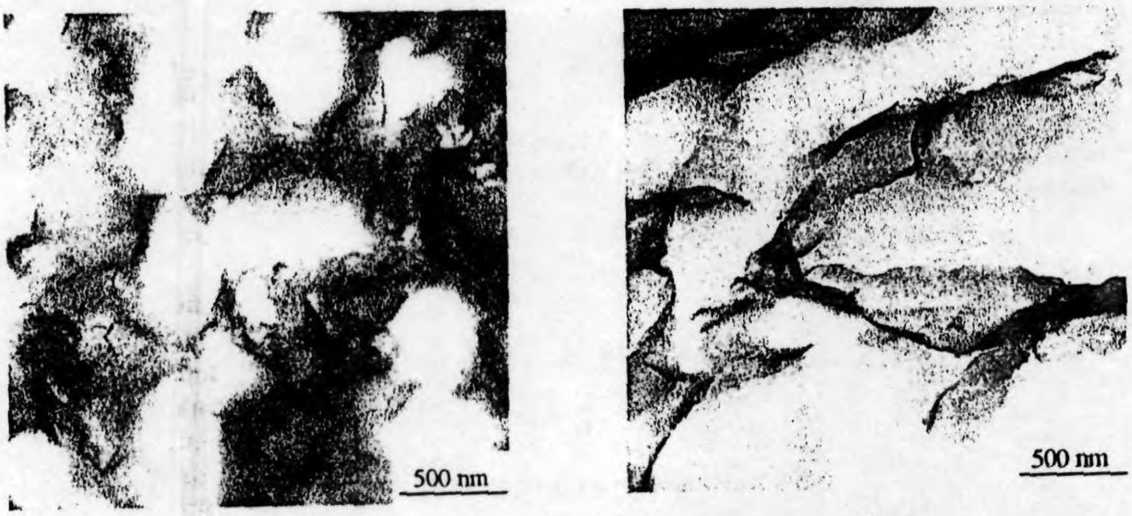
The presence of impermeable clay layers decreases the rate of transport by increasing the average diffusion path length in the specimen. The relative permeability compared to NR gum decreases in the order commercial clay (55%) > bentonite (35%) >fluorohectorite (5%). The penetration of the solvent molecule in to the composite is effectively prevented likely by the orientation of the clay layers. This indirectly shows that such composites are highly impermeable to solvents and gases.

3.4. Clay dispersion

The dispersion of layered silicate inside the composites was observed by TEM and are illustrated in Figures 5a and 5b, which represent bentonite and fluorohectorite filled NR vulcanizates respectively. In commercial silica filled composites, the filler exist as large particles. Recall that this clay was not a layered version. In bentonite filled vulcanizate there is some level of intercalation and the silicate layers form clusters (skeleton or house of cards structure) [4]. Here it can be seen that some level of filler network is formed which might be the reason for the high compound viscosity during mixing. However, in fluorohectorite filled nanocomposites, individual layers of the silicate are well discernible but they still form a skeleton structure. The exfoliation and dispersion of silicate layers can be better understood from the Figures 6a and 6b. In betonite (Figure 6a) filled composites bridging of silica nano-aggregates of very large aspect ratio forms a secondary filler network. This reinforcement structure explains the improvement in stiffness and strength. On the other hand, introduction of fluorohectorite (Figure 6b) in the NR results in a relatively large amount of exfoliated layers. Here clay layers are visible as regions of dark narrow bands within the polymer. Even though the layers are 'ceramic' in nature, because of their very large aspect ratio (ca. double of that of bentonite) and nanometer thickness, they behave mechanically more like sheets of paper rather than rigid plates [6]. This increased flexibility (elastic nature) of the layers contributes to the elasticity of the rubber. It has been reported that exfoliated clay layers orient along the strain direction in elastomers. This yields a further increase in the mechanical properties (strain hardening). It is believed that the formation of the skeleton-type silicate is favored by the rubber particle size of the latex. Note that this is only slightly changing owing to the vulcanization.

4. Conclusions

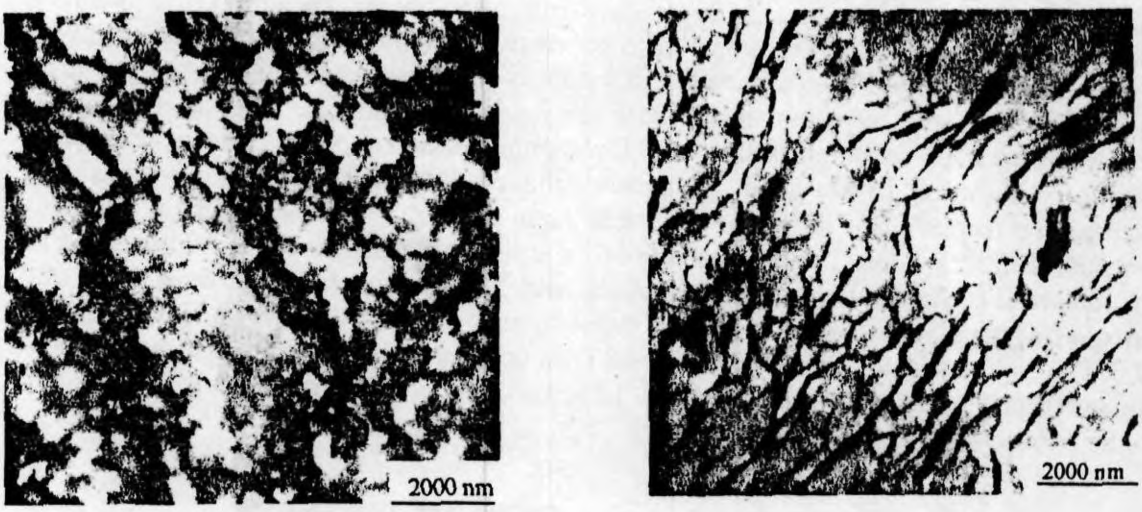
A suitable latex formulation has been designed for natural rubber latex and the conventional latex compounding method was used to produce vulcanized nanocomposites. Layered clays show excellent dispersion in NR compared to conventional composites. Layered clays filled NR vulcanizates exhibited a great increase in modulus and tensile strength especially in the case of fluorohectorite. Dynamic mechanical analysis reveled that the layered clay filled composites possessed very high stiffness and low damping characteristics. This was traced to be a reinforcing effect owing to intercalation/exfoliation and formation of a clay network structure. The formation of this clay network is likely favored by the initial rubber particle dispersion of the NR latex. Thermal stability of the layered silicates proved to be better than the commercial clay filled vulcanizates. Swelling, and TEM studies revealed some extent of orientation of the clay layers in the rubber. Exfoliation of the clay layers was demonstrated by TEM. Results indicate that the conventional latex compounding technique can be used to produce NR nanocomposites provided that the layered clay can form an aqueous dispersion with the NR latex.



5a

5b

Figures 5a-b. TEM pictures taken from different silicate filled fluorohectorite (nano)composites 5a) bentonite and 5b)Fluorohectorite



6a 6b

Figures 6a-b. Low magnification TEM pictures of the layered silicate filled (nano)composites with a) bentonite and b)Fluorohectorite.

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