

Dipping Characteristics of Layered Silicates–Natural Rubber Latex Nanocomposites

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ABSTRACT: The dipping characteristics of prevulcanized natural rubber latex containing three different types of silicates (fluorohectorite, bentonite, and English Indian clay) were studied using a semiautomatic dipping machine. The effect of variation in the speed of immersion and withdrawal of the glass former, dwell time, and concentration of the coagulant, etc. on the thickness of the latex deposit were investigated. Characterization of the composites was done using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The viscosities of these compounds were measured using a Brookfield viscometer. The results of the studies showed that the deposit thickness depends on the with-

drawal speed of the glass former, the concentration of the coagulant, dwell time, and the viscosity of the latex compound. Higher film thickness was noticed for the bentonite clay-filled composites. This was believed to be due to the formation of clay network formation in the composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 58–65, 2007

Key words: layered silicates; nanocomposites; natural rubber latex; prevulcanization; dry coagulant; immersion speed; withdrawal speed; dwell time

INTRODUCTION

Natural rubber latex is a macroscopic dispersion of rubber particles in an aqueous medium. This macroscopic viscous rubber medium (latex) is converted to elastic rubber through crosslinking of the macromolecules at their reactive sites (vulcanization). The introduction of organic accelerators in the vulcanization process enabled to reduce the vulcanization time and sulfur dose required for the optimum physical properties.^{1,2} This prevulcanized latex is an important raw material for the production of many dipped goods. Approximately 600,000 tonnes of latex concentrate is consumed in this way. In the case of dry rubber, carbon black and other inorganic minerals (clay, calcium carbonate, silicates, etc.) are used to improve the mechanical properties of the vulcanized rubbers. Carbon black offers excellent reinforcement owing to its strong interaction with rubbers, but at high loading, it decreases the processability of rubber compounds. The reinforcing capacity of silicates is poor because of the large particle size and low surface activity. Nowadays, there is great interest in the development of polymeric nanocomposite using layered silicates as reinforcing material.^{3–8} Provided that the layered silicates fully delaminate (exfoliation, a process in which clay plate-

lets, separate from one another in a polymer matrix) dispersing less than 10% of them may replace three to four times higher amount of traditional fillers without sacrificing the processability and mechanical properties. The concept of nano-reinforcement with layered silicates became very popular in late 1980s.^{8,9} Polymer nanocomposites represent a new alternative to conventionally (macroscopically) filled polymers. Because of their nanometer level dispersion, nanocomposites exhibit markedly improved properties when compared with pure polymers or traditional analogues. These include increased modulus and strength, outstanding barrier properties, improved solvent, heat resistance, and decreased flammability.^{9–12}

Layered silicate polymer nanocomposites are processable using latest technologies. Layered silicate is comprised of platelets (sheet-like structure of layered silicates where the dimensions in two directions far exceed the particles thickness) having a planar structure of 1 nm thick and 200–300 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 (nanometer scale) in a polymer matrix.¹⁰ 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)

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and dispersed (in which the silicate layers of ~ 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 to organophilic. This is the prerequisite for intercalation (process of diffusing the onium ions into the gallery space) 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 polymerization of monomers. This may strongly improve the strength of the interface between the silicate and the polymer.^{18,19}

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 possible because of rubber molecules.

In this study, the dipping characteristics of prevulcanized latex compounded with layered silicates were illustrated. Compounds were also prepared from an amorphous silica (English Indian clay) for comparison. Parameters such as viscosity, film thickness on rate of immersion and withdrawal of the glass former, and dwell time were studied in detail.

EXPERIMENTAL

Materials

Sodium fluorohectorite (Somasif ME-100) of Coop Chemicals, Japan is a synthetic layered silicate, which has an ion exchange capacity of 100 meq/100 g and an interlayer distance of 0.94 nm. Sodium fluorohectorite also exhibits a very high aspect ratio *viz.* 1000.^{16,17} Sodium bentonite (EXM 757) of Sud Chemie, Germany is a purified natural clay, having an ion exchange capacity and interlayer distance (space between the individual nanoclay platelets) of 80 meq/100 g and 1.24 nm, respectively. Commercial clay (English Indian Clays, India) has a cation exchange capacity of 8 meq/100 g and an interlayer distance of 0.72 nm.⁵ The formulations used for preparing prevulcanized latex are given in Table I. Centrifuged NR latex-high ammonia (HA)-type with 60% dry rubber content, conforming to Bureau of Indian Standards (BIS) specification 5430, was supplied by Rubber Research Institute of India. Sulfur, zinc diethyldithiocarbamate, and zinc oxide were supplied by Bayer, Germany and used as aqueous dispersions. Aqueous

TABLE I
Formulation of Prevulcanized Latex

Ingredients	Dry	Wet
60% Natural rubber latex	100	167
10% KOH solution	0.25	2.5
10% Potassium oleate	0.16	1.6
50% Sulfur dispersion	1.25	2.5
50% ^a ZDC dispersion	0.8	1.6
50% ZnO dispersion	0.25	0.5

^a ZDC, zinc diethyldithiocarbamate.

dispersions of layered clays were prepared with a special type of stirrer.

Prevulcanization of latex

For prevulcanization, the concentrated high ammonia (1%) latex having 60% dry rubber was mixed with the ingredients as listed in Table I, under slow stirring, at $55 \pm 1^\circ\text{C}$ for 4 h in a circulating water bath. Loss of ammonia during heating was compensated by adding (1%) freshly prepared ammonia solution. The prevulcanized latex thus obtained was cooled to room temperature and kept in sealed plastic containers. The prevulcanized natural rubber latex (PVNRL) was mixed with aqueous dispersion of silicates at different loading, after removing the dirt and coarse particles by filtering through a sieve (opening: 250 micron). It is then used for the dipping studies. The dipped films were dried at room temperature till transparent and vulcanized at 70°C for 2 h in an air-circulated oven. The vulcanized samples thus obtained were kept in a desiccator for mechanical testing.

X-ray diffractograms (XRD) were obtained from a D 500 diffractometer (Siemens, Munchen, Germany) using Ni-filtered CuK_α radiation ($\lambda = 0.1542$ nm). The samples were scanned in step mode at a scan rate of $1.5^\circ/\text{min}$ in the range $2\theta < 12^\circ$. The viscosity of the latex was measured at 25°C using a Brookfield viscometer (model-LV T, Stoughton, UK) with spindle number 2 at 60 rpm (ASTM D 2526-229). All the viscosity measurements were done prior to dipping. 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 .

Laboratory model dipping equipment supplied by DipTech (Stroud, UK) was used in this study. The machine has a dipping unit, which is suitable for products up to 430 mm in length. The dipping unit has two tanks, one for the latex and the other for the coagulant. Dipping can be performed either manually

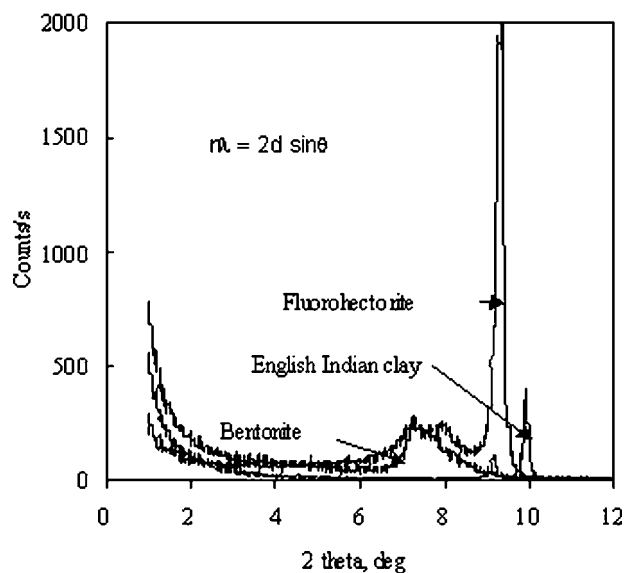


Figure 1 XRD spectrum of layered (bentonite and fluorohectorite) and nonlayered silicates (English Indian clay).

or automatically where we can control the speed of immersion as well as withdrawal. A digital micrometer supplied by Cadar Electronic (Sheffield, UK) was used for measuring the thickness of latex films.

Tensile tests were performed on a tensile tester (Zwick 1485, Germany) at a cross-head speed of 50 cm/min. For swelling studies, circular specimens (1.98 cm diameter and 0.20 mm thickness) were immersed in toluene at constant temperature (25°C) for 48 h. At equilibrium (as shown by constant weight of the sample), the samples were removed from the test bottles, adhering solvents was blotted off the surface, and the samples were weighed in airtight bottles on a sensitive electronic balance. The quantity of solvent absorbed was expressed as weight in grams of solvent absorbed by 1 g of the composite (swell index). The V_r values (volume fraction of rubber in the swollen gel) of samples were calculated using the Ellis and Welding equation.²⁰

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

Where D is the deswollen weight, F is the weight fraction of filler, A_0 is the solvent absorbed, T is the sample weight, ρ_r is the specific gravity of rubber (0.92) and, ρ_s is the specific gravity (0.86) of the solvent.

Dipping process

Rate of immersion of the glass former in PVNRL containing two different layered silicates (fluorohectorite and bentonite) and a nonlayered silicate on the thickness of the latex deposit was noted. A clean cylindrical glass former (diameter 25 mm and length 300 mm) was fixed on the former supporting bar of the dipping

machine and kept over the coagulant tank. A 10% solution of calcium nitrate as coagulant was taken in the coagulant tank. The former was then immersed in the coagulant by lifting the tank hydraulically at a speed of 100 cm/min. The former was then moved over to the tank containing compounded latex and dipped in it by raising the tank at a speed of 100 cm/min, and allowed to dwell for 30 s and then withdrawn (by lowering the tank) at the same speed. The former was inverted and rotated mechanically to obtain a uniform latex deposit on the former. The former was then dried to get a transparent film in the room temperature and vulcanized in an air-circulating oven at 70°C for 2 h. The former was then cooled, and the deposit was removed from the former by applying talc. The thickness of the deposit was measured with a digital micrometer having a sensitivity of 0.001 mm. The arithmetic mean of 10 measurements was taken as the thickness of the film. The speed of immersion of the former into the latex tank was changed to 110, 120, 130, 140, and 150 cm/min keeping all the other parameters constant and the thickness of the deposit was recorded. Similarly, the effect of other parameters like rate of withdrawal, dwell time, and concentration of the coagulant were also studied.

RESULTS AND DISCUSSION

XRD studies

The XRD spectrums of the layered silicates are 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.¹⁹ The XRD spectrum of fluorohec-

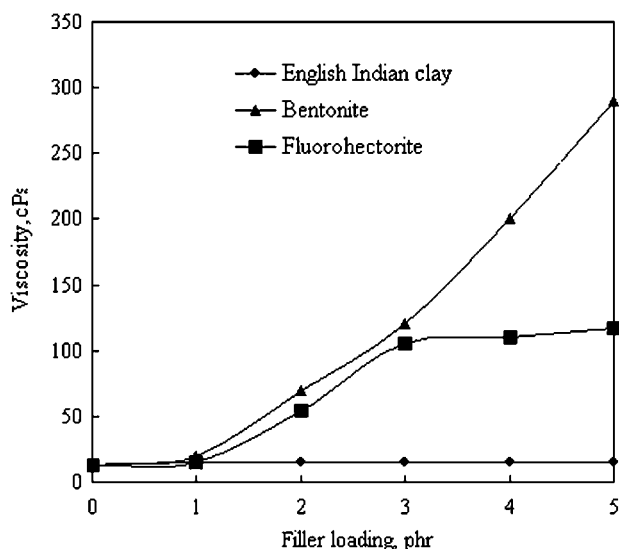


Figure 2 Viscosities of latex composites at different dosages of silicates.

torite showed three peaks, which from left correspond to interlayer distances 1.35, 1.24, and 0.96 nm, respectively. The strong peak at 0.96 nm indicate that majority of the layers in fluorohectorite have 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 $d = 0.72$ nm, which is not at all ideal for polymer intercalation as the interlayer distance is too small.⁵

Viscosity studies

Figure 2 shows viscosity of the latex compounds mixed with different silicates. The viscosity of latex compound has a critical role in most of the manufacturing processes. Bentonite incorporated latex compound showed higher viscosity than other fillers at all loading followed by fluorohectorite. When bentonite is mixed with water, it undergoes considerable swelling

due to hydration.¹ Because of this hydration, the initial interlayer distance increases that facilitates the intercalation of rubber molecules. Moreover, the ion-exchange capacity of bentonite is comparatively higher, which also influences the intercalation process. Fluorohectorite has higher cation exchange capacity and lower interlayer distance when compared with bentonite that registers viscosity values little lower than bentonite except at high loading. However, as the hydrogen bonds in English Indian clay are strong and the layers are resistant to swelling by hydration. Moreover, the very low cation exchange capacity (8 meq/100 mg) of English India clay makes it impossible to undergo any exchange reactions.

TEM studies

It will be interesting to analyze the TEM pictures of the composites. In Figure 3(a), the TEM of commercial

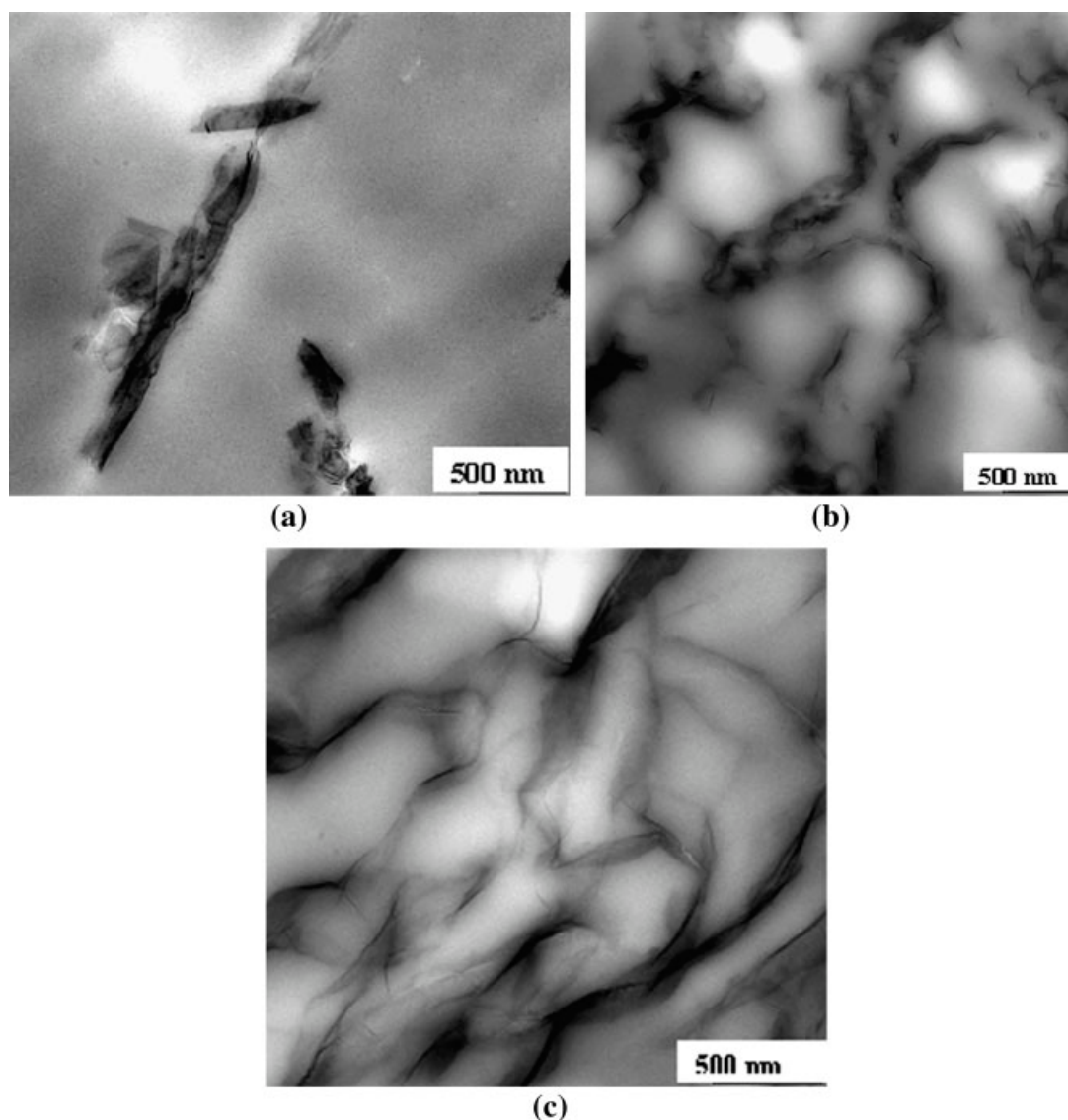


Figure 3 TEM pictures of (a) English Indian clay, (b) bentonite, and (c) fluorohectorite filled (nano)composites.

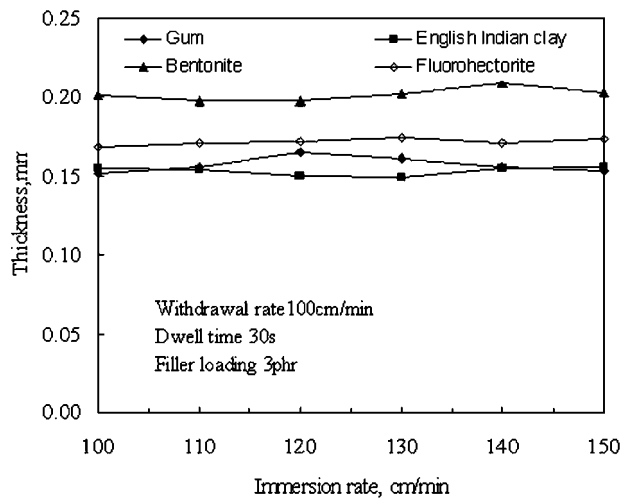


Figure 4 Effect of immersion rate on thickness of latex films at 3-phr loadings of different silicates.

clay (English Indian clay) loaded vulcanizate is given. Here the filler exists as large particles and the filler distribution is not homogeneous. This means, 10-phr loading of the commercial clay is not enough to saturate the polymer phase, as they exist as big particles distributed unevenly, which in effect weakens the matrix.¹³ However, in bentonite filled vulcanizate [Fig. 3(b)], the filler exists as a network of fine silicate layers around the rubber particles (white portion). This is because bentonite clay underwent some level of intercalation with rubber hydrocarbon, and the silicate layers form 'clusters or house of cards structure (bridge-like structure of exfoliated silicate layers).^{3,16} The high compound viscosity might be due to the formation of the layer network structure. The polymer phase is reinforced to a great extent as it is saturated

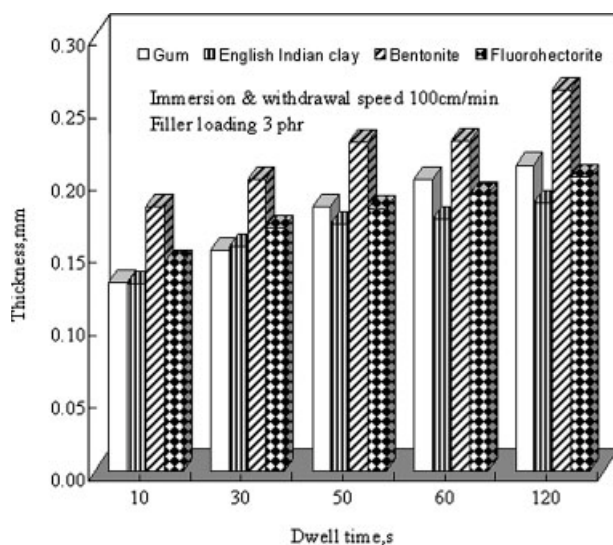


Figure 5 Effect of dwell time on thickness of latex films at 3-phr loadings of different silicates.

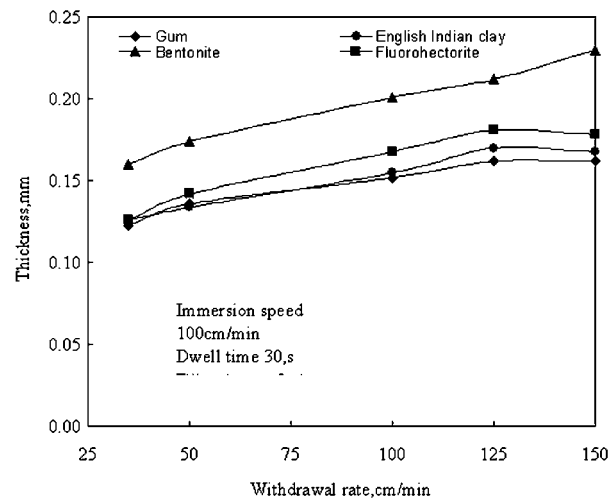


Figure 6 Effect of withdrawal rate on thickness of latex films at 3-phr loadings of different silicates.

with this network structure, which, in turn, contributed to greater mechanical properties to the vulcanizate. However, a fully saturated structure was observed in the case of fluorohectorite filled vulcanizate [(Fig. 3(c)]. Here, the silicate layers were intercalated to a greater extent¹⁶ and a small level of exfoliation was also observed, which exists as thin black strands in the photograph. The extent of exfoliation and the aspect ratio of the silicate layers are higher for fluorohectorite which might be the reason for the higher mechanical properties of fluorohectorite when compared with bentonite. Moreover, the exfoliated structure gives a several-fold increase in surface area.

Dipping studies

Figure 4 shows the variation in latex film thickness with the speed of immersion of the glass former at a

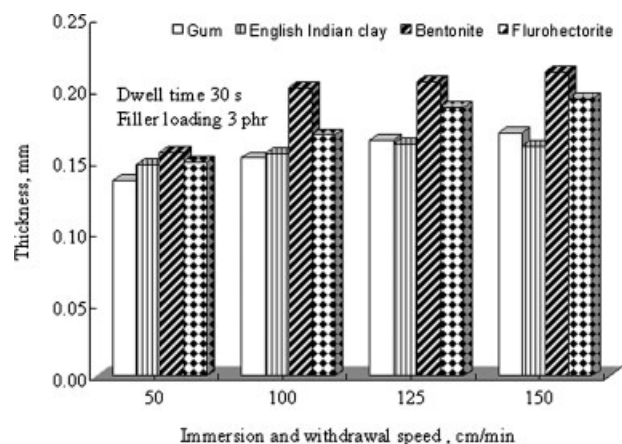


Figure 7 Effect of immersion and withdrawal rate (keeping them equal) on deposit thickness at 3-phr loading of different silicates.

TABLE II
Effect of Concentration of Coagulant on Deposit Thickness (mm) with Dwell Time

Dwell time (s)	English Indian clay (phr)				Bentonite (phr)				Fluorohectorite (phr)			
	0	1	3	5	0	1	3	5	0	1	3	5
10% Ca(NO ₃) ₂												
10	0.130	0.131	0.129	0.126	0.130	0.133	0.182	0.221	0.13	0.128	0.144	0.137
30	0.152	0.152	0.155	0.155	0.152	0.154	0.194	0.238	0.152	0.15	0.168	0.164
50	0.182	0.163	0.170	0.166	0.182	0.177	0.227	0.276	0.182	0.16	0.181	0.180
60	0.201	0.169	0.174	0.177	0.201	0.178	0.228	0.279	0.201	0.167	0.191	0.192
120	0.211	0.207	0.185	0.190	0.211	0.211	0.263	0.314	0.211	0.185	0.203	0.214
20% Ca(NO ₃) ₂												
10	0.160	0.158	0.160	0.173	0.160	0.165	0.207	0.249	0.160	0.153	0.152	0.174
30	0.192	0.195	0.192	0.222	0.192	0.211	0.248	0.284	0.192	0.183	0.197	0.197
50	0.225	0.228	0.243	0.237	0.225	0.225	0.257	0.290	0.225	0.209	0.215	0.223
60	0.235	0.231	0.248	0.252	0.235	0.262	0.290	0.315	0.235	0.216	0.221	0.235
120	0.282	0.273	0.271	0.287	0.282	0.293	0.314	0.334	0.282	0.260	0.263	0.249
30% Ca(NO ₃) ₂												
10	0.179	0.211	0.193	0.195	0.179	0.174	0.226	0.278	0.179	0.169	0.162	0.174
30	0.228	0.244	0.234	0.236	0.228	0.217	0.26	0.303	0.228	0.213	0.231	0.213
50	0.283	0.265	0.272	0.279	0.283	0.241	0.288	0.335	0.283	0.242	0.281	0.249
60	0.300	0.273	0.295	0.302	0.300	0.342	0.348	0.354	0.300	0.264	0.290	0.284
120	0.344	0.340	0.356	0.360	0.344	0.386	0.402	0.417	0.344	0.310	0.336	0.347

filler loading of 3 phr. As the speed of immersion increased from 100 to 150 cm/min, the thickness of the films show very little change at 1-phr loading (average film thickness 0.15 mm) of the silicates. Though the experiments were conducted with three different filler loading (1, 3, and 5 phr) the shape of the curves were almost identical and hence, the discussion was limited only to 3-phr loaded composite. As the filler loading was increased (Fig. 4) to 3 phr, the film thickness of bentonite filled compounds was higher than the other two versions. The film thickness are in the order bentonite > fluorohectorite > gum > English Indian clay.

Figure 5 shows the variation in thickness of the deposit with dwell time. As dwell time increased, the film thickness also increased. Initially, there was a gradual increase and thereafter the change is marginal. However, bentonite showed high film thickness at all points when compared with other clays. As the former with coagulant was immersed in latex, a layer of rubber coagulum was formed immediately, and as the dwell time increases, the coagulant ions get more time to diffuse into the latex to form a thick coagulum.^{21,22} Fluorohectorite showed slight increase in thickness, which ranged from 0.15 to 0.22 mm. However in the case of bentonite (5 phr), the thickness of the deposit increased considerably (0.22–0.32). This may be due to the greater volume of wet latex retained on the former due to the high viscosity of the compound.^{1,21,23}

Figure 6 shows the effect on the rate of withdrawal of the glass former on thickness of the deposit. As the rate of withdrawal increased, the deposit thickness increased slightly. At 3-phr loading the film thickness did not change considerably, except in the case of ben-

tonite (data not shown). As the withdrawal speed of the glass former from the latex compound increased, the time obtained to drain away the latex picked up on the former decreased, which resulted in a greater thickness to the deposit.^{22,23}

When the immersion and the withdrawal speed are equal, the change in deposit thickness are given in Figure 7. At higher speed, the deposit thickness increased. This might have been caused by the lesser drainage of the latex compound from the former. Table II shows the variation of dwell time and coagulant concentration on the deposit thickness. As the dwell time and the concentration of the coagulant increased, the deposit thickness increased. This is because as the concentration of the coagulant increased, the amount of coagulant deposit on the former increased and, hence the rate of diffusion of the coagulant into the latex was higher, which lead to a greater thickness.^{22,24,25}

Swelling behavior

Swell index values and V_r values of the composite are given in Tables III and IV. Table III shows the weight

TABLE III
Swell Index of Different Silicate Containing Vulcanizates

Silicate	Loading (phr)			
	0	1	3	5
Fluorohectorite	4.93	4.85	4.74	4.49
Bentonite	4.93	4.89	4.85	4.6
English Indian clay	4.93	4.90	4.89	4.83

in grams of toluene absorbed per gram of the composite at 25°C. The gum vulcanizate has the greatest toluene uptake at equilibrium swelling. This was expected as there was less restriction for the solvent absorption through 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 with fluorohectorite when compared with that containing commercial clay. In the case of layered silicates V_r values (Table IV) increased with filler loading, whereas for English Indian clay it decreased. The presence of impermeable clay layers decreased the migration by increasing the average diffusion path length in the specimen.²⁶ In commercial clay filled rubber, the solvent uptake is greater because of the weak interface and also due to poor clay dispersion.

Tensile properties

The tensile properties of four compounds are given in Table V. Here the effect of different silicates (at different loadings) on tensile strength, elongation at break, and modulus at 100 and 300% elongation are given. Tensile strength values decrease as the loading increases in the case of amorphous filler. This decrease may attribute to its high particle size. In the case of modulus also, almost similar behavior was observed. As the loading increases, the elongation at break of the amorphous filler increases. It is to be noted that at low elongation (100%) there is a gradual increase in modulus, which is in the order English Indian clay < bentonite < fluorohectorite. There is a superior increase in modulus with fluorohectorite at 300% elongation followed by bentonite. However, at the same elongation the magnitude of the modulus at 5-phr loading is higher when compared with that at 3-phr loading, especially with layered silicates. In the case of commercial clay-filled vulcanizates, this difference is negligible. The silicate layers may favor the formation of immobilized or partially immobilized polymer phases, which may contribute for high modulus.²⁷ In the vulcanizate containing layered silicate, a part of the silicate was exfoliated, which offered high surface area for reinforcement. The fine sheets of silicate layers orient along the strain direction, which increases with increased strain. The low stiffening

TABLE IV
 V_r Values of Different Silicate Containing Vulcanizates

Silicate	Loading (phr)			
	0	1	3	5
Fluorohectorite	0.1539	0.1548	0.1564	0.1612
Bentonite	0.1539	0.1546	0.1562	0.1603
English Indian clay	0.1539	0.1536	0.1525	0.1501

TABLE V
Tensile Properties of the Latex Film Vulcanizates

Properties	Loading (phr)			
	0	1	3	5
Tensile strength (MPa)				
English Indian clay	24.7	23.8	22.5	23.4
Bentonite	24.7	24.9	25.0	25.7
Fluorohectorite	24.7	25.0	25.8	26.6
Elongation at break (%)				
English Indian clay	837	842	850	1039
Bentonite	837	821	773	747
Fluorohectorite	837	810	782	732
Modulus at 100% elongation (MPa)				
English Indian clay	0.64	0.63	0.62	0.59
Bentonite	0.64	0.72	0.83	1.02
Fluorohectorite	0.64	0.84	0.90	1.10
Modulus at 300% elongation (MPa)				
English Indian clay	0.97	0.99	1.11	1.02
Bentonite	0.97	1.01	1.39	2.10
Fluorohectorite	0.97	1.23	1.75	2.14

effect of commercial clay can be attributed to its high particle size and poor dispersion.

CONCLUSIONS

The dipping characteristics of prevulcanized latex compounds containing layered silicates showed that they behave almost similar to conventional latex compounds. Parameters such as immersion rate, withdrawal rate, dwell time, and concentration of coagulant, etc. have found effect on film thickness. Bentonite, formed filler network showed higher compound viscosity and greater film thickness. The thickness of the deposit was found to increase with dwell time as well as increased concentration of coagulant. The thickness of latex deposit increased as the speed of withdrawal increased. Swelling studies revealed that fluorohectorite incorporated vulcanizate have high reinforcement. Superior mechanical properties were observed with layered silicate incorporated vulcanizates.

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