

# Rheological Behavior of Nanocomposites of Natural Rubber and Carboxylated Styrene Butadiene Rubber Latices and Their Blends

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**ABSTRACT:** Flow behavior of latices is industrially important for the manufacturing of various latex goods. Rheology of latices having fillers can assist in the understanding and quantification of the matrix–filler interaction. The impact of layered silicates such as sodium bentonite and sodium fluorohectorite on the rheological behavior of natural rubber, carboxylated styrene butadiene rubber latices, and their blends was analyzed with special reference to shear rate, temperature, and filler loading. The layered silicates-reinforced latex samples were characterized by X-ray diffraction technique to analyze the extent of intercalation and

exfoliation. In the presence of layered silicates, latex systems exhibited enhancement in viscosity due to the network formation. Because of the breaking of networks at higher temperature, the viscosity of all systems decreased with increase in temperature. Layered silicates-reinforced latex systems showed pseudoplastic flow behavior and possesses enhanced zero shear viscosity and yield stress. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2355–2362, 2006

**Key words:** latices; layered silicates; rheology; pseudoplastic

## INTRODUCTION

Fillers are used in latices to reduce the cost, to modify the viscosity, to impart color to the product, and also as reinforcing agent. Because of the absence of mastication step in the preparation of latex compounding, the filled latex goods exhibited inferior properties than dry rubber articles. One interpretation is that during mastication polymeric-free radicals are produced from the disintegrating rubber molecules, and that these radicals being very labile are able to interact with reactive sites on the surface of the filler particles, and so unite filler and rubber matrix into a bonded structure. This will not occur if the mastication step is absent. The commonly used fillers in latex industry include clay, whiting, silica, and carbon black. Recently, polymer-layered silicate (PLS) nanofillers have been extensively studied in industry because of their enhanced properties such as mechanical strength, thermal resistance, high gas barrier properties, etc.<sup>1–4</sup> The most commonly used layered silicates are montmorillonite, hectorite, and saponite. The important characteristics of layered silicates are its ability to disperse into individual layers and also their ability to

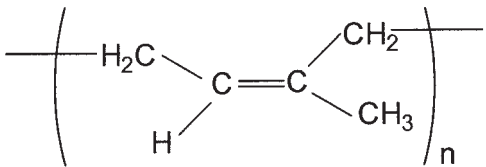
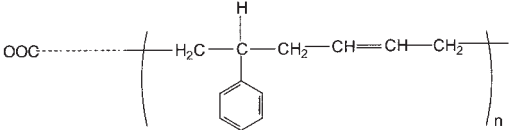
fine-tune their surface chemistry through ion-exchange reactions with organic and inorganic cations. According to the strength of interfacial interactions between the polymer matrix and layered silicates, three different types of PLS nanocomposites can be thermodynamically achieved and are as follows: (i) intercalated, (ii) flocculated, and (iii) exfoliated nanocomposites. Because of the high contact surface area, exfoliated system exhibits better properties. There are reported studies on the mechanical properties of latices with layered silicates.<sup>5,6</sup>

An understanding of the rheological properties of PLSNs is crucial to gain the fundamental knowledge of the processability and structure–property relations for these materials. Literature shows that the melt rheology has been utilized as a method to characterize polymer–clay nanocomposites.<sup>7–14</sup> Thomas and co-workers<sup>15–17</sup> studied the flow properties of natural rubber (NR)/styrene butadiene rubber (SBR) latex blends in the presence of surface active agents with reference to various parameters such as shear rate, temperature, and blend ratio.

This study deals with the rheological behavior of layered silicates-reinforced NR, carboxylated styrene butadiene rubber (XSBR), and 70/30 NR/XSBR latex polymeric systems. NR latex possesses high wet gel strength; it has low cost and has excellent physical properties. XSBR latex has better weather resistance, adhesion properties, and less permeable to gases and

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TABLE I  
Details of Latices Used

NR latex		
Supplied by		Gaico Rubbers, Kuravilangadu, Kottayam
Dry rubber content (DRC) (%)		60
Total solid content (TSC) (%)		61.25
XSBR latex (PLX-802)		
Supplied by		Apar Industries, Bombay, India
Dry rubber content (DRC) (%)		47
Total solid content (TSC) (%)		50.66
Styrene content (%)		52

solvent molecules. Blending of these two polymers will result in new systems with better physical properties. It is important to mention that as compared to synthetic latices NR latex is highly viscous. Sodium bentonite and sodium fluorohectorite are the nanofillers used for this study. The activation energy, pseudoplasticity index, zero shear viscosity, and yield stress of the filled samples have been analyzed.

## EXPERIMENTAL

Details of latices used for the rheological studies are given in Table I. The vulcanizing agents and accelerators used were procured from M/s Bayer India, Mumbai, India. The synthetic-layered silicate sodium fluorohectorite of interlayer distance 0.94 nm was collected from Coop Chemicals, Japan, and the purified natural clay sodium bentonite having interlayer distance 1.24 nm from Sud Chemie, Germany. The characteristics of layered silicates are shown in Table II.

Prevulcanization of latices was carried out by heating the compounded latex (in accordance with the formulation given in Table III) using water bath at 70°C for 2 h. A 10% aqueous dispersion of layered silicates was added

into the latex in varying amount with slow stirring. It was then filtered through a 250- $\mu$ m mesh size sieve for removing the impurities. The weight percentage of layered silicates used 1, 1.5, 2, and 2.5% for hundred parts of rubber. Higher loading of layered silicates showed thickening effect and hence lower weight percentage of silicates was selected. Since there are so many samples with varying parameters such as clay systems, different loading, etc., a basic coding system has been adopted throughout this study. In the code *N* stands for NR, the subscripts 100, 70, and 0 indicate weight percentage of NR, sP denotes sulfur prevulcanization, and E and F represents sodium bentonite and sodium fluorohectorite, respectively. The subscript numbers 1.0, 1.50, 2.0, and 2.5 indicate the weight percentage of E and F.

X-ray diffraction patterns were taken by using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.154$  nm) by X'pert diffractometer, Philips, at 40 keV and 30 mA. The samples were scanned in step mode by 1.5°/min scan rate in the range of  $2\theta < 12^\circ$ .

The rheological measurements were carried out using Haake Viscotester VT 550. Coaxial cylinder sensors according to ISO 3219 type were used for the measurements. The experiments were done at 25°C for all the samples over a range of shear rate. The samples with 2.5 phr fillers were carried out at different temperatures such as 25, 35, and 45°C.

TABLE II  
Characteristics of Layered Silicates Used

Trade name	Chemical name	Ion-exchange capacity (mequiv./100 g)	Layer distance (nm)
Somasif ME-100	Na-fluorohectorite	100	0.94
EXM 757	Na-bentonite	80	1.24

## RESULTS

### Characterization of latex nanocomposites

The extent of exfoliation and intercalation of polymer into the layers of silicates is obtained from X-ray dif-

**TABLE III**  
**Formulation of Latex Mixes**

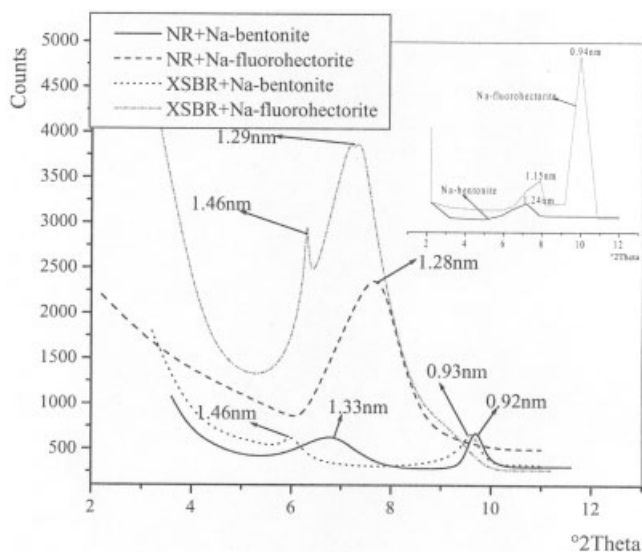
	N <sub>100sP</sub>	N <sub>70sP</sub>	N <sub>0sP</sub>
60% Centrifuged NR latex	100	70	–
47% XSBR latex	–	30	100
10% Potassium hydroxide solution	0.25	0.25	0.25
50% Sulphur dispersion	1.5	1.5	1.5
50% ZDC dispersion	0.75	0.75	0.75
50% ZMBT dispersion	0.5	0.5	0.5
50% Zinc oxide dispersion	0.2	0.2	0.2
10% Sodium bentonite dispersion	1, 1.5, 2, 2.5	1, 1.5, 2, 2.5	1, 1.5, 2, 2.5
10% Sodium fluorohectorite dispersion	1, 1.5, 2, 2.5	1, 1.5, 2, 2.5	1, 1.5, 2, 2.5

ZDC, zinc diethyl dithiocarbamate; ZMBT, zinc mercaptobenzothiazole.

fraction pattern. The change in interlayer spacing, i.e., the *d*-spacing of the latex nanocomposites is observed from the peak position in the XRD graphs in accordance with Bragg equation:

$$n\lambda = 2d \sin \theta \tag{1}$$

where *n* is an integer,  $\lambda$  is the wavelength, *d* is the interlayer spacing, and  $\theta$  is the angle of diffraction. The X-ray diffraction pattern of the layered silicates and latex nanocomposites are given in Figure 1. The interlayer spacing of latex nanocomposites is found to increase with the incorporation of clay. In the case of exfoliated structure, layer separation associated with the delamination of the silicate structure in the polymer matrix, leading to the disappearance of X-ray scattering. It may be due to either the presence of an extremely large regular ordered spacing between the layers or the nanocomposite that no longer has an ordered layer structure.

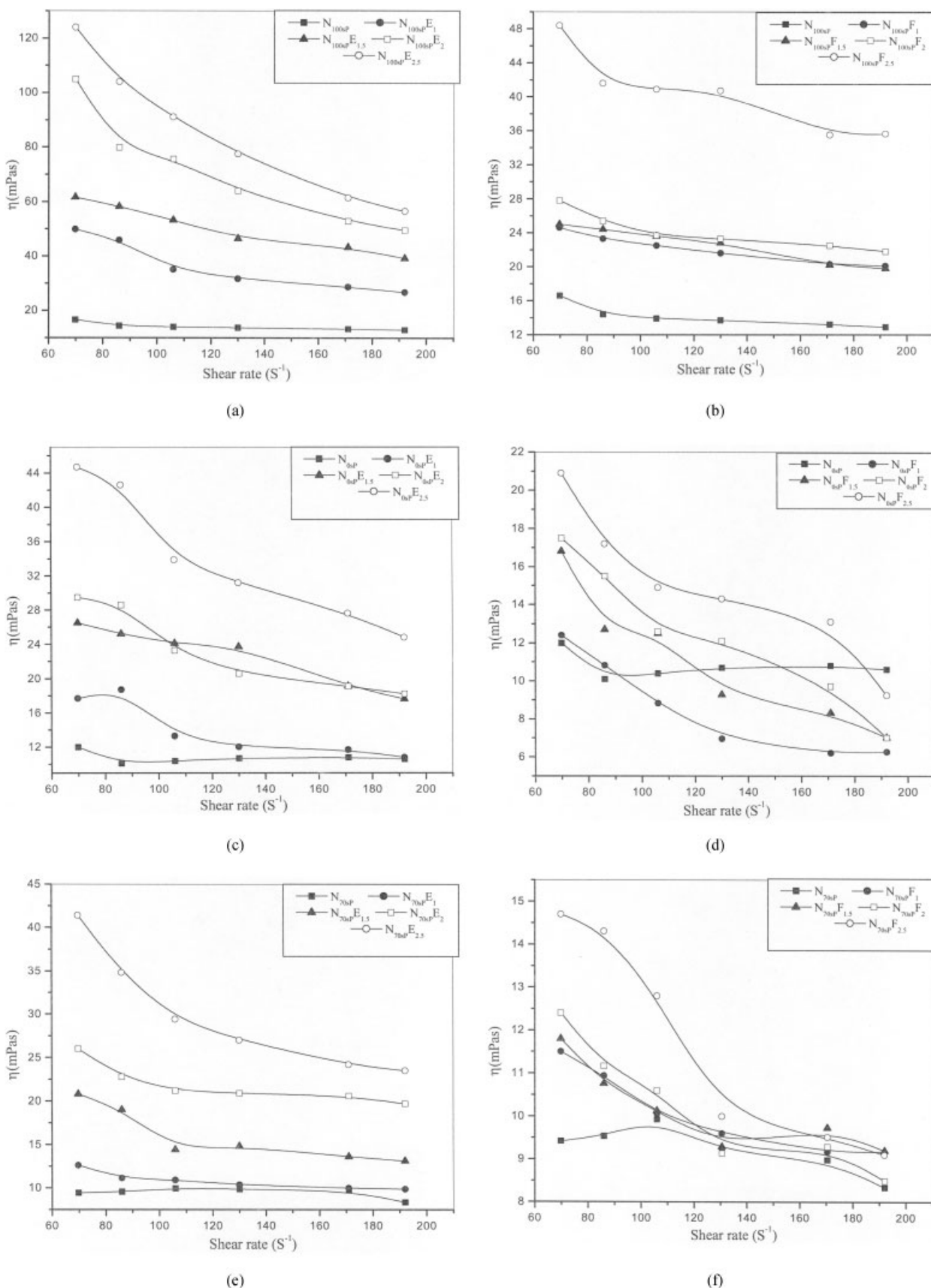


**Figure 1** X-ray diffraction patterns of layered silicates and latex nanocomposites.

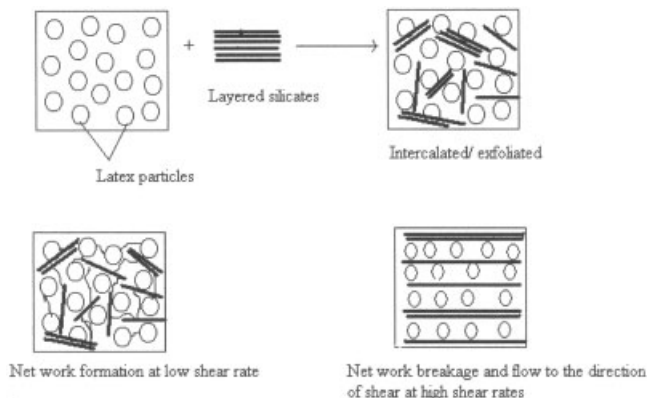
**Rheological measurements**

The rheological behavior of polymer nanocomposites has been studied by several researchers<sup>18,19</sup> because the knowledge of it is essential for polymer processing and to design the end products. The dynamic oscillatory and steady-shear rheology studies of polymer nanocomposites revealed the enhanced viscosity values as compared to pristine and can be attributable in terms of the formation of a intercalated or exfoliated network structure by clay platelets.<sup>20–23</sup> The flow properties of sodium bentonite and sodium fluorohectorite-filled NR, XSBR, and 70/30 NR/XSBR latices have analyzed with reference to shear rate, filler loading, and temperature. Figures 2(a)–2(f) are the shear rate versus viscosity curves of sodium bentonite and sodium fluorohectorite latices and their blend at various filler loading. In all the systems, the viscosity of layered silicates-reinforced latex samples decreases with increase in shear rate, representing pseudoplastic nature, i.e. shear-thinning behavior. The change in networks of latex nanocomposites with shear rate is presented schematically in Figure 3. Figure 4 shows that the viscosity of latices increases as a function of weight percentage of filler. The increase in viscosity is owing to the reinforcement occurred in the system in the presence of layered silicates because of the high polymer/filler interaction. The extent of reinforcement of layered silicates can be analyzed using Kraus equation.<sup>24</sup> Kraus plots of sodium bentonite- and fluorohectorite-filled latex nanocomposites are given in Figures 5(a) and 5(b). The negative slope values obtained for Kraus plots are pointing to the reinforcement of filler in the polymer matrix (Table IV).

Because of the breakage of networks, the viscosity decreases with increase in temperature [Figs. 6(a) and 6(b)]. The activation energy of the latex nanocomposites is determined from Arrhenius plots. The activation energy and zero shear viscosity of layered silicates-reinforced latex nanocomposites are shown in Table V. It is found that the activation energy and zero shear viscosity of filled samples are higher than virgin polymers. This can be explained in terms of the en-



**Figure 2** Effect of shear rate of the viscosity of (a) NR+E, (b) NR+F, (c) XSBR+E, (d) XSBR+F, (e) 70/30 NR/XSBR+E, and (f) 70/30 NR/XSBR+F.

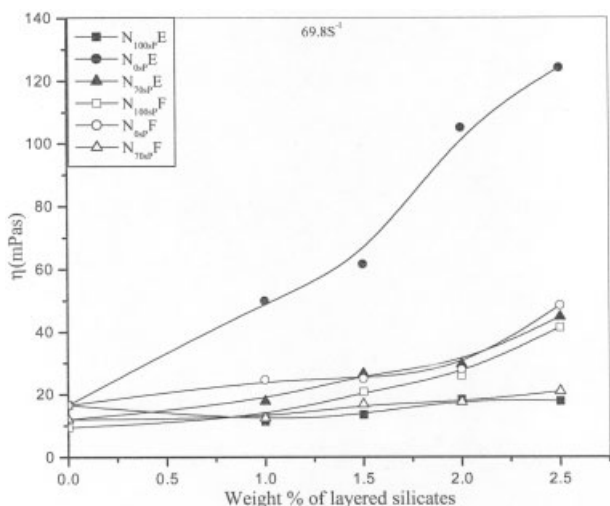


**Figure 3** Schematic representation of influence of shear rate on network formation and breakage.

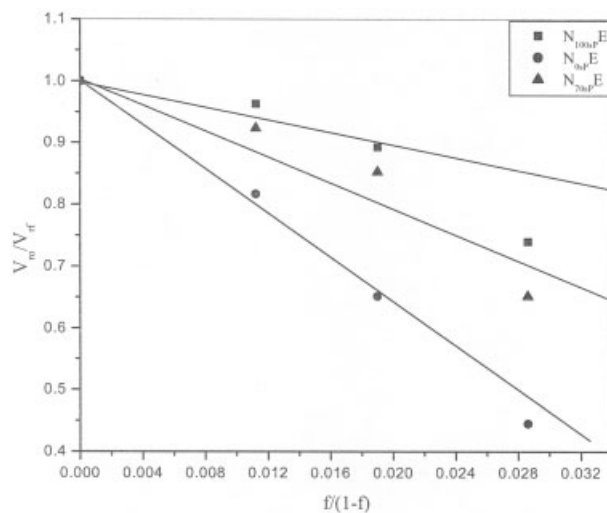
hancement in polymer/filler interaction because of high aspect ratio of layered silicates. Table VI gives the pseudoplasticity index and yield stress values of latex nanocomposites. In all cases, the filled latex sample shows more pseudoplasticity than virgin polymers owing to the formation of networks at low shear rate and the breaking of all networks at higher shear rates.

**DISCUSSION**

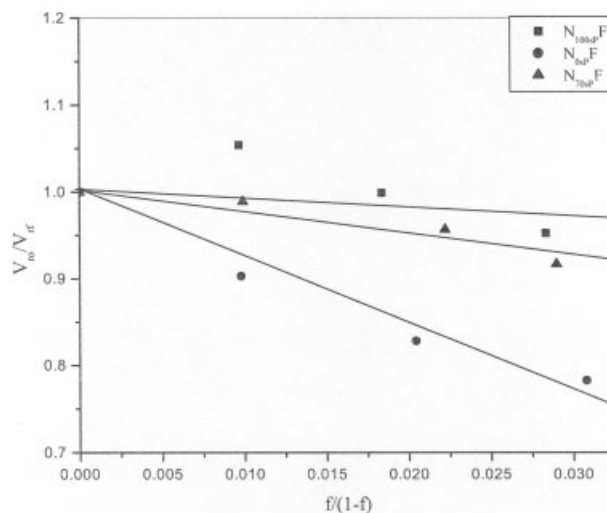
X-ray diffraction method has been used to characterize the formation and structure of polymer–silicate hybrids by monitoring the position, shape, and intensity of the basal reflection from the silicate layers. When insertion of polymer chains in the silicate layers occurs, an increase of silicate inter-layer volume and corresponding layer spacing gives rise to the shifting of diffraction peaks to lower angles. Diffraction peak cannot be seen in the case of exfoliated structures where silicate layers are com-



**Figure 4** Variation in viscosity with concentration of layered silicates in NR, XSBR, and 70/30 NR/XSBR.



(a)



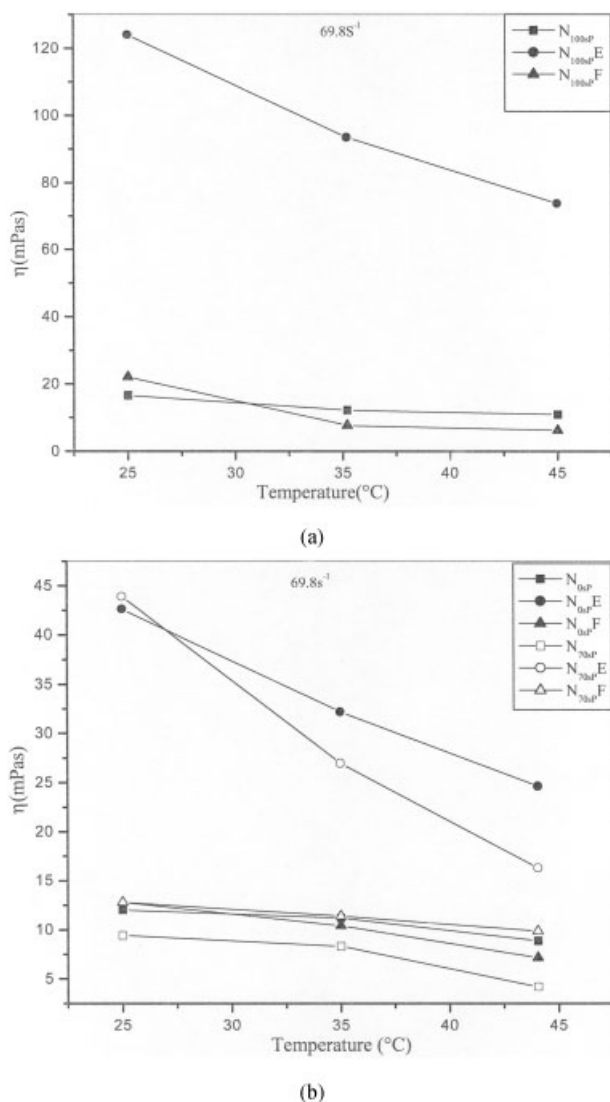
(b)

**Figure 5** Kraus plots of nano fillers reinforced latex nanocomposites (a) sodium bentonite and (b) sodium fluorohectorite.

pletely and uniformly dispersed in a continuous polymer matrix. Figure 1 is the diffractograms of layered silicates and latex nanocomposites. Sodium bentonite clay exhibits a single peak at an angle  $2\theta$

**TABLE IV**  
The Slope  $m$  Values from Kraus Plot

Sample	Kraus equation slope ( $m$ )
$N_{100pE}$	-8.96
$N_{0sE}$	-19.48
$N_{70sE}$	-11.84
$N_{100pF}$	-2.09
$N_{0sF}$	-7.04
$N_{70sF}$	-2.78



**Figure 6** Effect of temperature on the viscosity of latex nanocomposites (a) NR and (b) XSBR and 70/30 NR/XSBR.

of  $7^\circ$ , corresponding to a basal spacing of 1.24 nm. The synthetic silicate sodium fluorohectorite has two peaks at  $2\theta$  of  $8^\circ$  and  $9.5^\circ$ , corresponding to a

**TABLE V**  
Activation Energy and Zero Shear Viscosities of Filled (2.5phr) and Unfilled Latex Systems

Sample	Activation energy (KJ/mol)	Zero shear viscosity ( $\eta_0$ ) (mPas)
N <sub>100sP</sub>	19.76	18.18
N <sub>100sPE</sub>	31.12	135
N <sub>100sPF</sub>	58.79	52.5
N <sub>0sP</sub>	13.98	13
N <sub>0sPE</sub>	26.6	46
N <sub>0sPF</sub>	9.63	23
N <sub>70sP</sub>	37.63	8.87
N <sub>70sPE</sub>	23.45	45.4
N <sub>70sPF</sub>	18.88	15

**TABLE VI**  
Pseudoplasticity Index and Yield Stress Values of Filled (2.5 phr) and Unfilled Latex Systems

Sample	Pseudoplasticity index ( $n$ )	Yield stress (Pa)
N <sub>100sP</sub>	0.92	1.04
N <sub>100sPE</sub>	0.23	8.76
N <sub>100sPF</sub>	0.87	1.67
N <sub>0sP</sub>	0.72	0.88
N <sub>0sPE</sub>	0.32	3.30
N <sub>0sPF</sub>	0.44	0.69
N <sub>70sP</sub>	1.06	0.68
N <sub>70sPE</sub>	0.51	2.9
N <sub>70sPF</sub>	0.68	0.98

basal spacing of 1.15 and 0.94 nm, respectively. XRD pattern of sodium bentonite (E) filled NR shows peaks with an interlayer spacing of 1.33 and 0.92 nm. The characteristic interlayer spacing obtained for fluorohectorite filled NR sample is 1.281 nm. Sodium bentonite filled XSBR exhibits the basal reflections at an interlayer distance of 1.46 and 0.93. Sodium fluorohectorite-filled XSBR exhibits interlayer distance of 1.29 and 0.94 nm. From Figure 1 it is found that in all systems the interlayer spacing increases because of the intercalation of polymer into the layers of layered silicates. Enhanced interlayer distance indicates that the layered structure is retained in the clay system because of the formation of intercalated nanocomposite. Varghese and Karger-Kocsis<sup>24</sup> have investigated the dispersion of layered silicates in NR latex. They observed that commercial clay particles exist as large particles while layered silicates shows intercalated structure.

The flow properties of the latex samples were analyzed using Ostwald's (Power law) equation:

$$\tau = K \dot{\gamma}^n \quad (2)$$

where  $\tau$  is the shear stress,  $\dot{\gamma}$  is the shear rate,  $n$  is the pseudoplastic index, and  $K$  is the viscosity index. Viscosity is calculated using the equation:

$$\eta = K \dot{\gamma}^{n-1} \quad (3)$$

The flow behavior of latex nanocomposites depends on the degree of compatibility between polymer matrix and the clay. Moreover, the interlayer distance of the clay should also play an important role in determining the dispersion of layered silicates in latices and hence the viscosity.<sup>2</sup> As expected the viscosity of all latex nanocomposites increases with the addition of layered silicates. The rheological behavior of polymer suspensions depends on liquid binding or immobilization mechanism. It means that the polymers dispersed in the aqueous medium are immobilized within the layers of layered silicates. It is well known

that the layered silicates has the ability to separate the layers and can intercalate the polymers between the layers. According to Lazzeri et al.<sup>18</sup> the polymer molecules that get immobilized in the filler surface are considered as a contribution to the dispersed phase with the effect of raising the effective filler volume fraction. Since at each shear rate there is a structural equilibrium between the immobilized and mobilized part, the effective volume fraction is a function of shear rate. This is the reason behind the shear thinning behavior of layered silicates-reinforced latex samples. From the viscosity curve it is clear that latex nanocomposites have non-Newtonian behavior. As the shear rate increases, the viscosity of the samples decreases. The shear thinning behavior is predominant in these samples as the filler loading increases, which indicates the network formation at low shear rate and its gradual destruction at higher shear rates. The schematic model explains the formation of networks and its breakage at higher shear rates (Fig. 3). The viscosity change is predominant for sodium bentonite-filled NR, XSBR, and 70/30 NR/XSBR than fluorohectorite-filled samples. This can be ascribed by the formation of filler networks of bentonite during compounding. However, fluorohectorite silicates form more exfoliated structure in the polymer. We know that fluorohectorite is synthetic clay and its cation-exchange capacity is higher than bentonite (Table II). As a result the interfacial tension between the polymer and the filler decreases. According to Varghese and Karger-Kocsis,<sup>24</sup> the formation of filler network due to the intercalation of polymer chain into the layers might be the reason for the increase in viscosity.

Owing to the high aspect ratio and layered structure of the silicates, the viscosity of latex increases as a function of weight percentage of filler (Fig. 4). Because of the nanometer size of filler dispersions, the nanocomposites exhibit markedly improved properties as compared to pristine polymers. The extent of reinforcement in latex systems occurred in the presence of these layered silicates is estimated from Kraus plot.<sup>25</sup> The Kraus equation is given by

$$\frac{V_{ro}}{V_{rf}} = 1 - m \left( \frac{f}{1-f} \right) \quad (4)$$

A plot of  $V_{ro}/V_{rf}$  against  $f/(1-f)$  shows the extent of reinforcement caused by fillers in various polymeric materials. In eq. (4),  $V_{ro}$  is the volume fraction of rubber phase in swollen gel of gum rubber vulcanizate and is given by

$$V_{ro} = \frac{d/\rho_p}{d/\rho_p + A_s/\rho_s} \quad (5)$$

where  $V_{ro}$  is constant for a particular system.

$V_{rf}$  is the volume fraction of rubber phase in swollen gel of filled rubber vulcanizate and is calculated using equation

$$V_{rf} = \frac{(d-fw)/\rho_p}{d-fw/\rho_p + A_s/\rho_s} \quad (6)$$

where  $d$  is the deswollen weight,  $f$  is the volume fraction of the filler,  $w$  is the initial weight of the sample,  $\rho_p$  is the density of the polymer,  $\rho_s$  is the density of the solvent, and  $A_s$  is the amount of solvent absorbed. For an unfilled system  $f = 0$ ,  $m$  is the slope of the Kraus plot and its value gives the interaction of matrix and filler.

The Kraus plot of E- and F-filled NR, XSBR, and 70/30 NR/XSBR are presented in Figures 5(a) and 5(b). According to this theory, the negative slope ( $m$ ) values are an indication of reinforcement of filler in the matrix. Layered silicates-reinforced systems exhibit negative slope values because of the higher reinforcing capability of layered silicates occurred by the intercalation of polymer into the layers of silicates. The values of  $m$  are given in Table IV. The higher the degree of reinforcement of layered silicates in rubber matrix, the higher the negative  $m$  values.

The effect of temperature on the viscosity of latex nanocomposites is shown in Figures 6(a) and 6(b). Viscosities of all systems decrease with increase in temperature. As the temperature increases the networks get easily broken and as a result the flow units become less restricted and less organized.<sup>17</sup> The sharp decrease in the viscosity of bentonite-filled NR, XSBR, and 70/30 NR/XSBR is associated with the temperature-induced breakdown of the filler networks. The effect of temperature on the flow behavior of layered silicates-reinforced latices is further analyzed from the Arrhenius plots using the equation:

$$\eta = \eta_0 e^{-E_a/RT} \quad (7)$$

where  $E_a$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is the absolute temperature.

The activation energy of individual latices and their blend in the presence of layered silicates (2.5 phr) are given in Table V. The activation energy of filled NR latices is higher than the pristine polymer, indicating the high temperature sensitivity of the material due to the intercalation of layered silicates in the polymer. In the case of XSBR, sodium bentonite-filled system exhibits higher activation energy than fluorohectorite-filled and virgin polymer because of the network formation of filler. In the case of blends, the nanofilled systems show reduction in activation energy as compared to the unfilled sample. The unexpected decrease in temperature sensitivity of the blend system can be explained in terms of the uneven distribution of layered silicates in the two phases.

The zero shear viscosity ( $\eta_0$ ) of the layered silicates-reinforced samples is higher than the virgin polymers (Table V). The sharp increase in  $\eta_0$  for filled systems indicates the enhancement in polymer/filler interaction due to high aspect ratio of layered silicates.

The shear thinning exponent,  $n$  is a semiquantitative measure of the degree of exfoliation and delamination. The extent of non-Newtonian behavior of polymeric materials is obtained from its flow index values. The pseudoplastic, dilatant, and Newtonian behavior of polymers are characterized by the values of  $n$ , i.e.,  $n < 1$ ,  $n > 1$ , and  $n = 1$  correspondingly. The flow index values of latices are shown in Table VI. The pseudoplasticity of NR, XSBR, and 70/30 NR/XSBR are found to increase by the addition of layered silicates. The increase in pseudoplastic behavior indicates a higher extent of silicate exfoliation on nanoscale with a macroscopic preferential orientation of the layers. However, unfilled 70/30 NR/XSBR exhibits dilatant behavior at low shear rate because of the network formation in the blend system on applying force. However, at higher shear rate the viscosity decreases because of the rupturing of networks.

Yield stress of a polymeric material can be considered as a measure of the additional shear stress arising from the presence of interparticle interactions. The colloid does not start to flow until a critical, i.e., yield stress is reached at which the network begins to break apart. In a weakly flocculated system, the yield stress can be related to the energy required to separate aggregated particles into single units. The yield stress corresponds to the maximum force per unit area that the network can withstand before rupturing. Table VI shows the yield stress values of unfilled and filled (2.5 phr) NR, XSBR, and 70/30 NR/XSBR latex systems. In all the systems the yield stress values of latices containing layered silicates are higher than unfilled samples. However, the  $\tau_0$  value of XSBR with fluorohectorite clay is lower than its gum sample because of its plasticization effect at lower concentration of filler.

## CONCLUSIONS

Latex nanocomposites were characterized by X-ray diffraction technique. The diffraction pattern obtained revealed that the intercalation of rubber chains into the silicate galleries occurred during mixing. The rheological behavior of NR, XSBR, and their blend in the presence of layered nanosilicates was analyzed with special reference to shear rate, filler loading, and temperature. It was found that the viscosity of the latices with layered silicates increased as a function of concentrations of filler and also exhibited pronounced shear thinning behavior. Enhancement in viscosity upon the addition of nanofillers indicated a more uniform distribution of clay particles and higher extent of silicate exfoliation on nanoscale. The extent of reinforcement of clay layers in rubber was analyzed from

the Kraus plot. The negative value of the slope supported the reinforcing ability of layered silicates in latex.

As the temperature is increased the viscosity of all samples decreased because of the rupturing of network existed between rubber and filler. It was observed that the activation energy of layered silicates-reinforced NR latex is higher than other samples because of the intercalation of polymer into the layers of silicates, thereby enhancing the temperature sensitivity of the material. Zero shear viscosity of layered silicates-filled latices was higher than unfilled samples due to the enhancement in contact surface area between polymer and the filler. In the present study, latices containing layered silicates possess lower  $n$  values, which indicated a higher degree of exfoliation. Latex nanocomposites exhibited higher yield stress values as compared to gum and can be interpreted in terms of the intercalation/exfoliation of layered silicates in rubber.

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