Rheological Behaviour of Layered Silicate–Natural Rubber Latex Nanocomposites

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SUMMARY

The rheological behaviour of prevulcanised natural rubber (NR) latex nanocomposites based on layered silicates such as sodium bentonite and sodium fluorohectorite was studied. A typical commercial clay (non-layered version) was chosen as the reference. The effect of layered silicates on flow properties was analysed by investigating latex viscosity as a function of shear rate, temperature, and filler loading. In the presence of layered silicates, latex compounds show enhanced viscosity, probably owing to a network formation of silicate layers in the latex phase. The shear thinning behaviour exhibited by the nanocomposites at high temperature may be due to the network breakdown of silicate layers. Latex–layered silicate systems show pseudoplastic behaviour and increased zero shear viscosity and yield stress.

Keywords: layered silicate; nanocomposite; natural rubber latex; rheology

INTRODUCTION

In recent years, much attention has been paid to polymer nanocomposites based on layered silicates (LS) having platelets with nanometer dimensions [1–8]. The layers cannot be separated from each other through general rubber processing techniques. The most commonly used layered silicates are montmorillonite (MMT), hectorite, and saponite. The important characteristic of layered silicates is their ability to disperse into individual layers. According to the strength of interfacial interaction between polymer matrix and layered silicates, three different types of polymer-layered silicate are thermodynamically

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possible: (1) intercalated; (2) flocculated; (3) exfoliated. Owing to the high surface area, exfoliated systems exhibit better properties.

A deep knowledge of the flow behaviour of compounds containing layered silicates is essential to understand the processability and structure property relations of the materials. The viscosity of latex plays a critical role in the flow and shaping behaviour of latex compounds. Several investigations have been made to understand the rheological behaviour of polymers in view of their relevance to processing [9–12].

Melt rheology has been utilised as a method to characterise polymer–clay nanocomposites. Thomas and coworkers have studied the flow properties of NR/SBR latex blends in the presence of surface-active agents with reference to various parameters such as shear rate, temperature, and blend ratio [13, 14]. The flow properties of compounded latices are strongly influenced by shear rate, particle size, presence of electrolytes, temperature, etc. Prevulcanised natural rubber latex has been an industrially important raw material for the production of many latex articles such as condoms, catheters, gloves, etc. It has a very low residual chemical content, and the various tailor-made forms make it suitable for the production of many latex articles. Data regarding the processing and rheological behaviour of nanocomposites are very important in designing end-products [15, 16]. The rheological behaviour of prevulcanised natural rubber latex modified with different types of layered silicate will be analysed in this paper.

EXPERIMENTAL

Materials

The latex for the rheological studies were procured from the Rubber Research Institute of India, Kottaym, Kerala, which conforms to the BIS specification (**Table 1**). The vulcanising agents and accelerators were supplied by Bayer (India) Ltd, Mumbai, India. The synthetic layered silicate used was sodium fluorohectorite (Somasif ME-100) of Coop Chemicals, Japan, which has an ion-exchange capacity of 100 meq/100 g and an interlayer distance of 0.94 nm. It also exhibits a very high aspect ratio (= 1000) [5, 6]. Sodium bentonite (EXM 757) of Sud Chemie, Germany, is a purified natural clay having an ion-exchange capacity of 80 meq/100 g and an interlayer distance of 1.24 nm. The details of the commercial clay (English Indian Clays, India) used are given in **Table 2**. The formulation used for preparing the latex compound is given in **Table 3**. Aqueous dispersions (10%) of layered silicates were prepared with

Table 1. Specifications of concentrated latex (BIS 5430-1981)

Properties	Value	Requirements
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, s	1000	475[a]
Volatile fatty acid number	0.02	0.15[b]
Coagulum content by mass, %	0.03	0.05[b]
Copper, ppm	1	8[b]
Manganese, ppm	Traces	8[b]

[a] *Minimum*
[b] *Maximum*

Table 2. Details of the English Indian clay

English Indian clay	Content, %
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 in ignition	15.47

Table 3. Formulation of the latex compound

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

a special type of stirrer. The concentrated high-ammonia latex with 60% dry rubber was mixed with the ingredients as listed in **Table 3** under slow stirring. The above latex compound was mixed with aqueous dispersions of silicates at different levels of loading. The dirt and coarse particles were removed by filtering through a sieve (opening 250 μm). The compounds were then used for rheological studies. The rheological measurements were carried out using a Haake-VT 550 viscometer (Germany).

This viscometer consists of a steel cup attached to a temperature-controlled system, a cylindrical sensor and a rotor, which can be rotated at preset speeds. After pouring latex into the gap between the cup and the cylindrical sensor, and running the rotor at a preset speed, the viscosity of the latex compound was measured. The sample exerts a resistance to the rotational movement (owing to its viscosity), which becomes apparent as a torque applied on the measuring shaft of the VT 550. The torque required to maintain the set speed is proportional to the viscosity. From the torque developed, the set speed, and the geometrical factors of the sensor, the viscosity, shear stress, and shear rate were calculated with the help of built-in software.

In the present study, 9 mL of latex compound was pipetted out into the gap between the cup and the sensor system. The temperature was set at the desired value in the range 25–45°C, and the speed of rotation was varied to obtain shear rates in the range 1–200 s^{-1}. The apparent viscosity (mPa s), shear rate (s^{-1}), and shear stress (Pa) were read directly from the machine.

RESULTS AND DISCUSSION

Rheological Measurements

Dynamic oscillatory and shear rheology studies of the layered-silicate-modified latex revealed enhanced viscosity compared with that of latex modified with conventional clay, which can be attributed to the formation of an intercalated or exfoliated network structure of clay platelets [17–20]. The rheological behaviour of latex nanocomposites has been analysed using Ostwald's power-law equation [21]:

$$\tau = k\dot{\gamma}^n$$

where τ is the shear stress (Pa), k is the viscosity index, $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the pseudoplasticity index. The n and k values were obtained by regression analysis of the values of τ and $\dot{\gamma}$ obtained from experimental data. The apparent viscosity (η) was calculated using the equation:

$$\eta = k(\dot{\gamma})^{n-1}$$

Each rheogram was analysed for yield stress (τ_0), viscosity index (k), and pseudoplasticity index (n).

The variations in viscosity with shear rate for fluorohectorite, bentonite, and English Indian clay at 25°C are given in **Figure 1**. The flow behaviour of latex nanocomposites may show the degree of compatibility between the polymer matrix and the layered silicate. Moreover, the interlayer distance of the clay also plays an important role in the intercalation and hence the viscosity. It is found that viscosity decreases with shear rate for all silicates, and higher viscosity values are registered by layered silicates (fluorohectorite and bentonite). The interlayer distance of fluorohectorite is 0.94 nm, and that of bentonite 1.25 nm. However, the cation-exchange capacity of fluorohectorite and bentonite are 100 and 80 respectively. In dispersions, greater exchange reactions are possible with fluorohectorite because the CEC is higher. In dispersion, fluorohectorite undergoes hydration, which further increases its interlayer distance, and the exchange reaction is faster with fluorohectorite than with bentonite. When the latex is mixed with the layered silicate dispersion, rubber molecules can easily intercalate in between the layers. As a result, the viscosity of layered

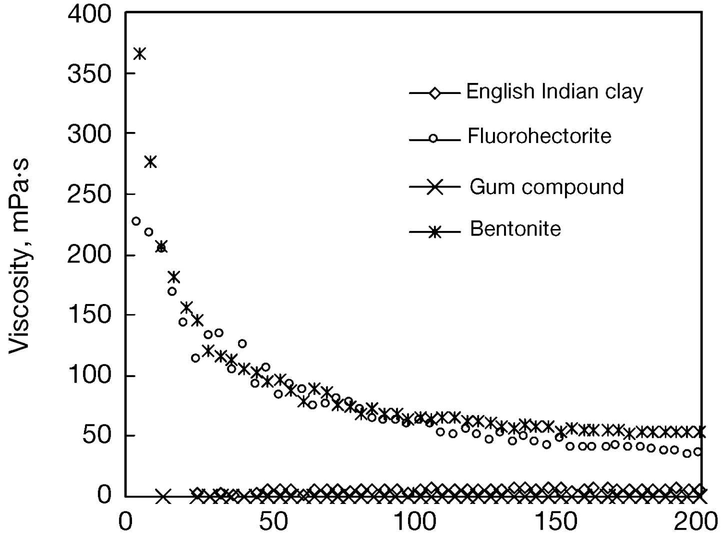

Figure 1. *Effect of viscosity on shear rate of NR latex nanocomposites at 5 phr loading, temperature 25°C*

silicate–latex mix is higher than that of the control or of the corresponding non-layered version.

The rheological behaviour of polymer suspensions depends on their liquid binding or immobilisation mechanism. The polymer dispersed in the aqueous phase is immobilised within the layers of silicates. It is well known that the layered silicate has the ability to separate the layers and can intercalate the polymers in between the layers. According to Lazzeri and coworkers [15], the polymer molecules, when immobilised in the filler surface, are considered to contribute to the dispersed phase, with the effect of raising the effective filler volume fraction. As, at each shear rate, there is a structural equilibrium between the immobilised and mobilised part, the effective volume fraction is a function of shear rate. This may be the reason behind the shear thinning behaviour of layered-silicate-reinforced latex samples. From the viscosity curve it is clear that layered-silicate-modified latex exhibits non-Newtonian behaviour.

The variations in viscosity with shear rate at 5 phr loading of different silicates can also be seen in **Figure 1**. Here, the gum latex sample and the commercial-clay-modified latex do not show any change in viscosity with shear rate. However, the shear thinning behaviour is obvious in the case of layered silicate compositions at higher loadings, which indicates network formation at low shear rate and its linear alignment along the shear direction at higher shear rates. The viscosity of the latex compounds is found to increase on the addition of silicates. It can be seen that, at low shear rates, the filled latex compounds show much higher viscosity than the unfilled compound. The difference narrows down at higher shear rates. The restriction offered by the fillers to Brownian movement of the latex particles seems to be overcome at higher shear rates. A schematic model can explain the formation of networks, and the orientation of the exfoliated or intercalated structure along the shear direction at higher shear rates is shown in **Figure 2**. The network formation of layers in the nanocomposites at low shear rates and their orientation along with the rubber molecules are illustrated in the scheme.

The variation in viscosity with shear rate at different temperatures is given in **Figure 3**. Owing to the non-Newtonian behaviour, a single viscosity measurement of latex at a particular temperature is not enough to understand its flow behaviour. The study was conducted at three different temperatures, 25, 35, and 45°C, which represent the conventionally adopted temperature range for the manufacture of latex goods. The viscosity shows only minor changes with temperature, which might be due to the small differences in the selected temperatures. However, at 45°C there is a sudden increase in viscosity ($>50\ s^{-1}$), which may be due to the coagulation of latex at high temperature and shear rate. As the temperature increases, the network becomes aligned

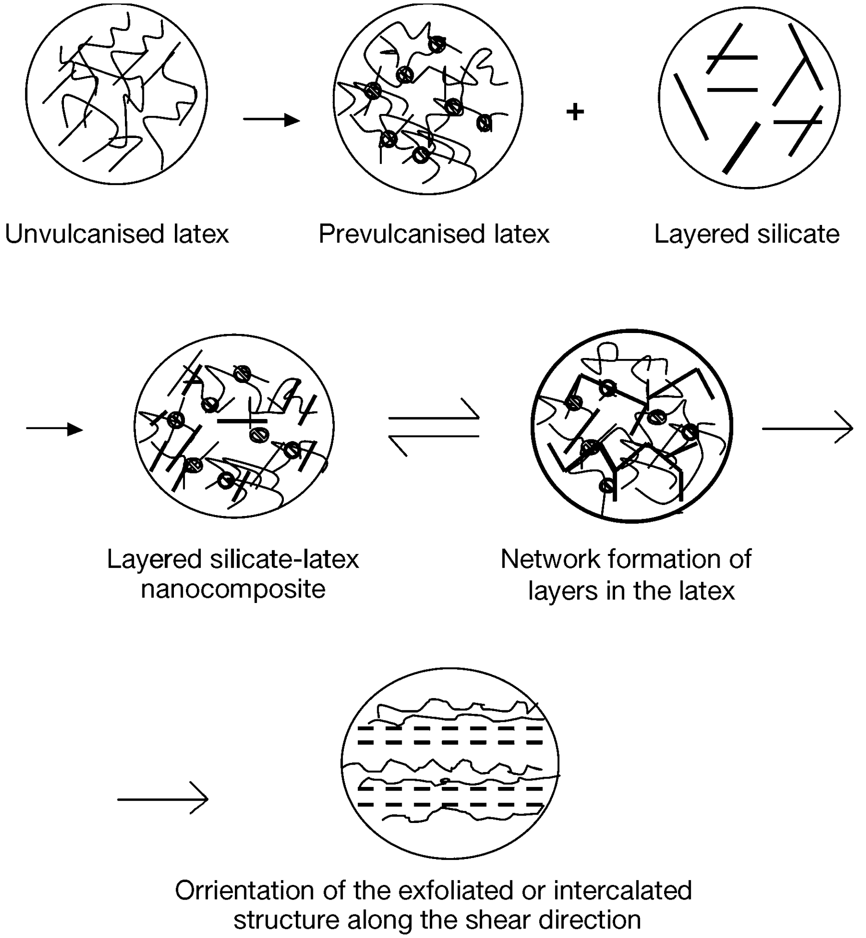

Figure 2. *Schematic representation of rubber hydrocarbon and layered silicate and their alignment in the shear direction*

so that the free volume is increased, and as a result the flow units become less restricted and less organised [22]. At 1 phr loading of fluorohectorite, the viscosity rises first and then remains almost constant with increase in temperature (data not given). In all systems, the viscosity of layered-silicate-reinforced latex samples decreases with increase in shear rate, indicating a pseudoplastic nature or shear thinning behaviour.

However, in the case of fluorohectorite-modified latex (**Figure 4**), the change in viscosity with change in temperature is negligible. The process stability and consistency at elevated temperature are much better with fluorohectorite

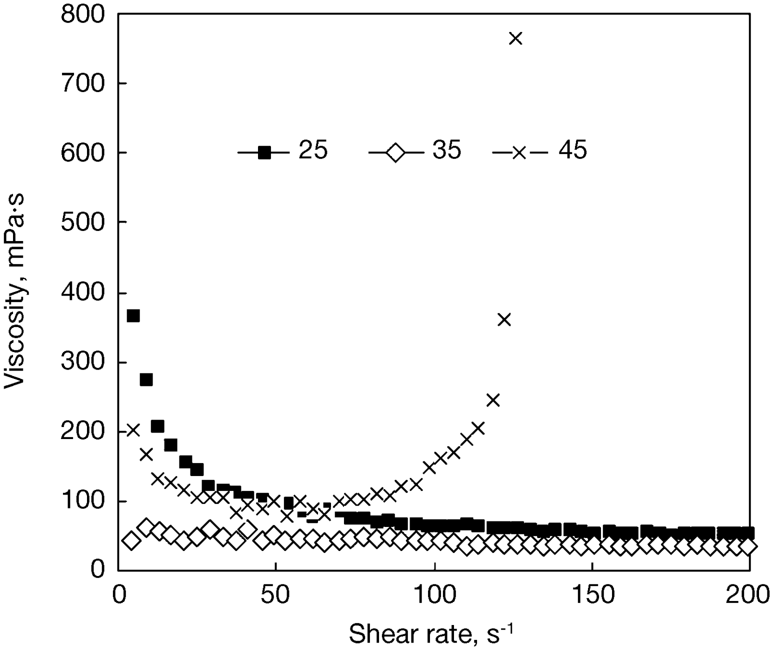

__Figure 3.__ Effect of viscosity on shear rate of bentonite nanocomposites at different temperatures (5 phr loading)

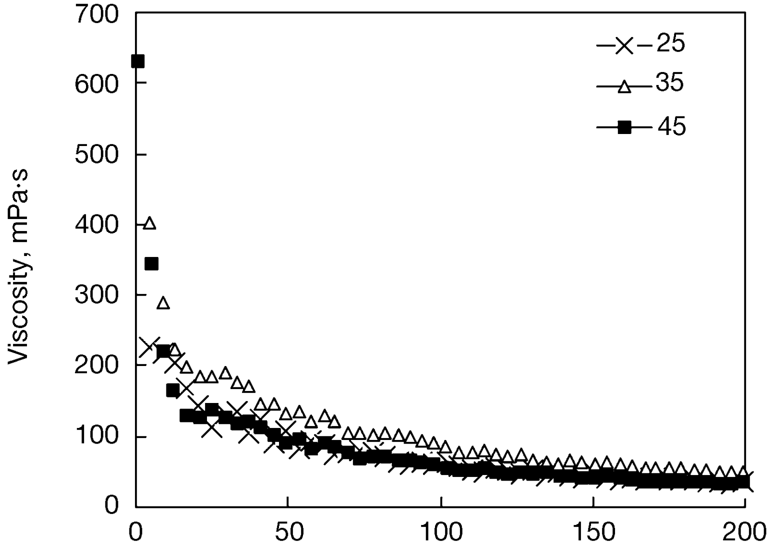

__Figure 4.__ Effect of viscosity on shear rate of fluorohectorite nanocomposites at different temperatures (5 phr loading)

than with bentonite. This may have practical significance in heat-sensitised dipping of prevulcanised latex nanocomposites. The effect of the viscosity of the latex at different loadings of fluorohectorite at 25°C is given in **Figure 5**. There is a steady increase in viscosity with higher levels of fluorohectorite. For every nanofiller there is a threshold level above which the filler particles agglomerate in the medium, which leads to poor mechanical properties. It has been found that, for an NR latex–fluorohectorite system, 3 phr loading is sufficient for reinforcement [23]. At 5 phr loading of fluorohectorite there is structure formation at low shear rates ($>75\ s^{-1}$), whereas at high shear rates shear thinning occurred.

The viscosity changes for different silicates at a shear rate of 78 s^{-1} are given in **Figure 6**. Initially there is very little change in viscosity, whereas higher viscosity values were recorded for further addition of the layered silicates. However, this change is minimum with English Indian clay (non-layered version). The surface area of non-layered silicate is 80 m^2/g, whereas the effective surface area in a partially exfoliated system is 790 m^2/g. This accounts for the higher viscosity of the layered silicate–latex system. The restriction offered by the filler to Brownian movement of the latex particles seems to be overcome at higher shear rates.

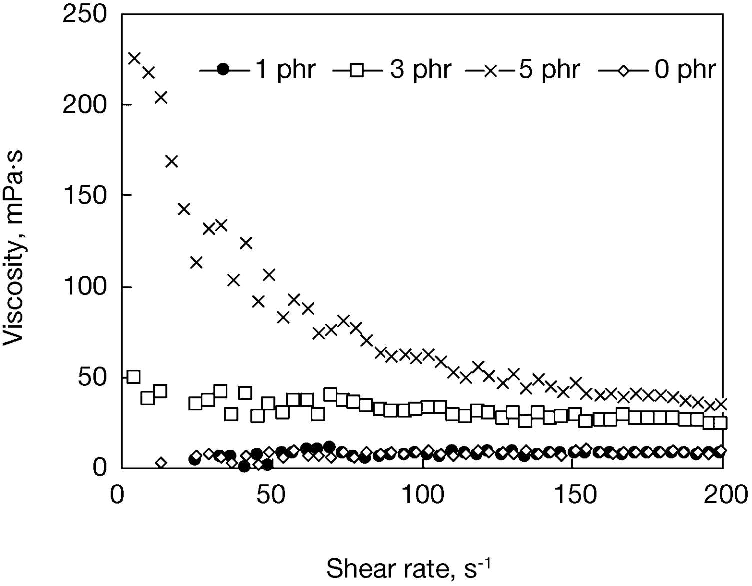

Figure 5. *Effect of viscosity on shear rate of fluorohectorite nanocomposites at different loadings (temperature 25°C)*

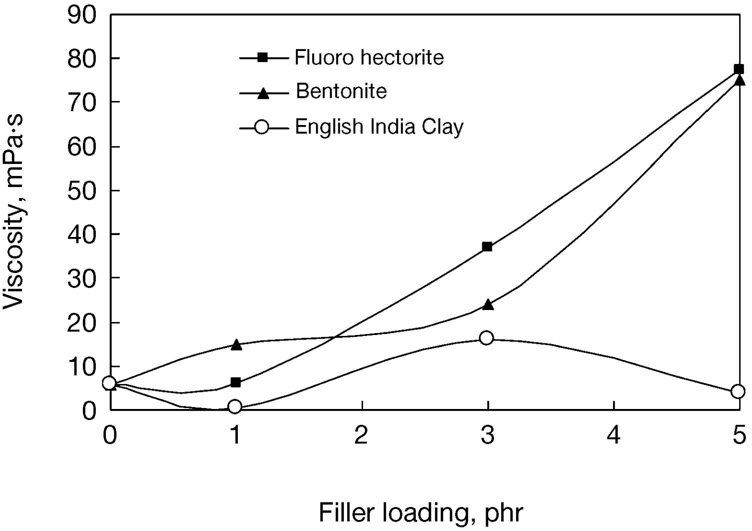

Figure 6. Effect of viscosity on filler loading of NR latex nanocomposites at a shear rate of 78 s^{-1}

Activation Energy (E_a)

The effect of temperature on the viscosity of latex nanocomposites is shown in **Figure 7**. The viscosities of all systems decrease with increase in temperature as the networks collapse and the flow units become less restricted and organised. The effect of temperature on the flow behaviour of layered-silicate-reinforced latices can be further analysed from Arrhenius plots using the equation:

$$\eta = \eta_0 \ e^{-E_a/RT}$$

where E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. The Arrhenius plot at a specific shear rate (95 s^{-1}) and at 5 phr loading is given in **Figure 8**. The activation energies of different silicates at 5 phr loading at a specific shear rate (95 s^{-1}) were calculated and are given in **Table 4**. From this it is clear that the activation energy is higher for layered silicates than for the gum compound and the commercial clay. This may be due to the higher intercalation of the layered silicates.

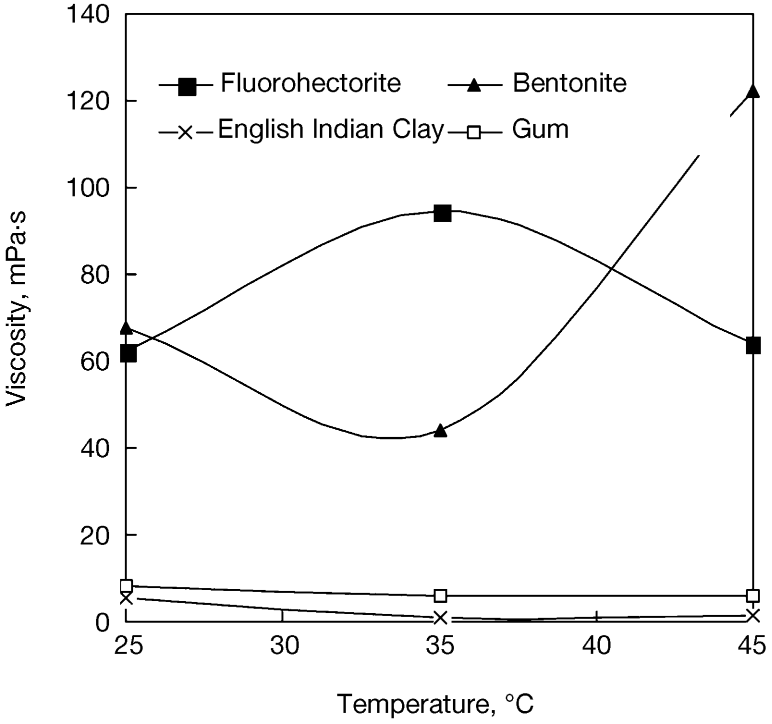

Figure 7. *Effect of viscosity on temperature of NR latex nanocomposites at 5 phr loading (shear rate 95 s^{-1})*

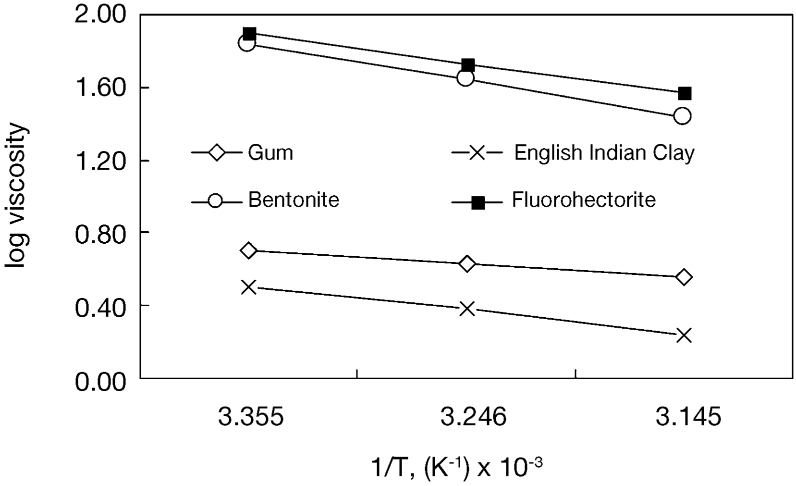

Figure 8. *Arrhenius plots of nanocomposites at 5 phr loading (shear rate 95 s^{-1})*

Table 4. Activation energy at a shear rate of 95 s^{-1} (filler loading 5 phr)

Sample	Activation energy(kJ/mol)
Gum compound	80.15
English Indian clay	151.60
Bentonite	222.38
Fluorohectorite	186.18

Zero Shear Viscosity (η_0)

Figure 9 shows the effect of filler loading on zero shear viscosity at 25°C. The general trend observed is a decrease in zero shear viscosity with temperature. This was associated with the temperature-induced molecular network breakdown. It was also noticed that η_0 of nanocompounds shows a sharp increase compared with η_0 of the gum compound and the English Indian clay compound. This shows the significance of a high aspect ratio and polymer–filler intercalation/exfoliation on viscosity.

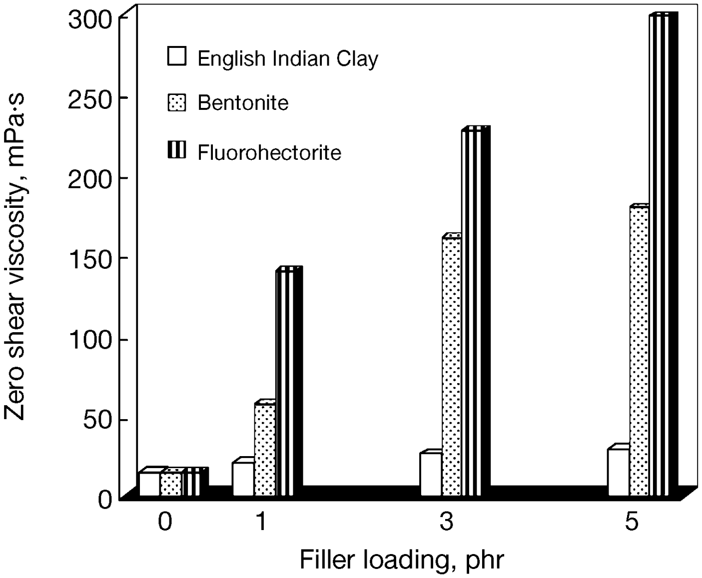

***Figure 9.** Zero shear viscosity versus filler loading at 25°C*

Yield Stress (τ_0)

Figure 10 shows the effect of filler loading on yield stress at 25°C. The yield stress (τ_0) of a polymer can be assessed as a measure of the outcome of extra

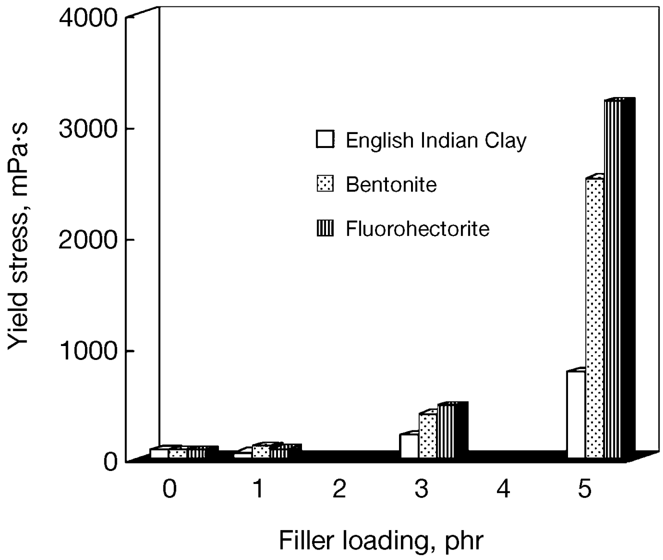

Figure 10. *Yield stress versus filler loading of latex nanocomposites at 25°C*

shear stress due to interparticle interactions. There is an initiating force to start the flow in a colloid. Therefore, a finite stress is to be applied to initiate the flow in these systems. At that point the network begins to break down. Thus, the flocculated system containing aggregated particles divided into single units. Yield stress represents the maximum value of force per unit area that the network can withstand before breaking down. The nanocomposites show higher values of yield stress at all three temperatures than the virgin compound and the compound with English Indian clay; the filler loading does not make much difference.

Pseudoplasticity Index (*n*)

Natural rubber latex is a pseudoplastic fluid, and, when sheared, the rubber particles are progressively aligned and offer less resistance to flow. Thus, the apparent viscosity of the latex decreases on increasing shear rate and continues to do so until the flow curve becomes linear. The extent of non-Newtonian behaviour of the system can be rated from the *n* values. The effects of temperature and filler content (5 phr) on the flow behaviour indices of the samples are given in **Table 5**. The pseudoplastic, dilatant, and Newtonian behaviour of polymers is characterised by the values $n < 1$, $n > 1$, and $n = 1$ respectively. A high value of *n* shows a less pseudoplastic nature of the material. The increase in pseudoplasticity shows a higher extent of silicate exfoliation associated with network build-up of the layers.

Table 5. Pseudoplasticity index (n) of nanocomposites at 5 phr loading

Sample	Pseudo plasticity index (n)		
	Temperature, °C		
	25	35	45
Gum compound	0.93	0.86	0.76
Fluorohectorite	0.42	0.406	0.38
Bentonite	0.39	0.346	0.29
English Indian clay	0.79	0.71	0.66

Figure 11 shows the stress–strain curves of various silicate-loaded composites at 5 phr loading. As the shear rate increases, the shear stress also increases in all cases. In the case of gum and English Indian clay there is not much increase in stress values, but in the case of nanofillers there is a very notable change, especially in the case of bentonite. This may be because of the network formation and the stress for the alignment of the filler–polymer network. The fine sheets of silicate layers generated by exfoliation align along the direction of the rubber hydrocarbon at elevated stress.

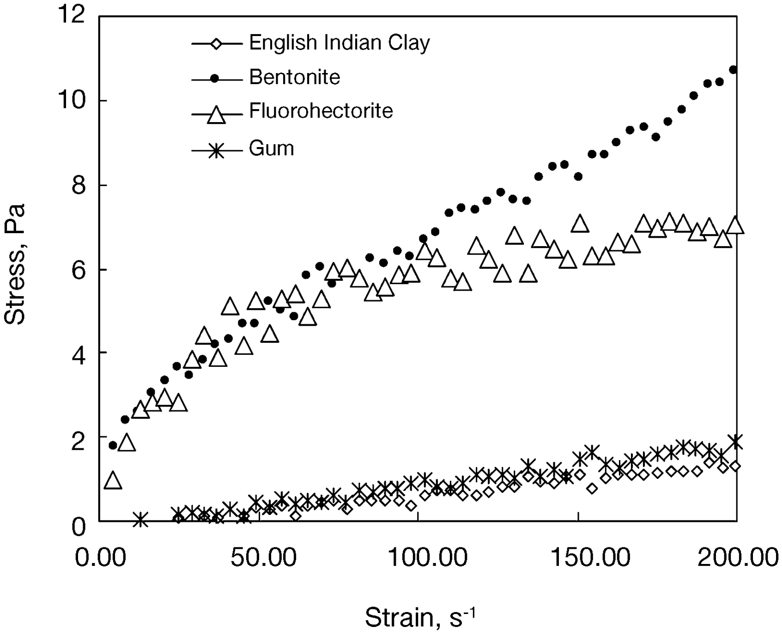

Figure 11. *Stress–strain curves of latex nanocomposites at 5 phr loading of layered silicates (temperature 25°C)*

CONCLUSIONS

The flow behaviour of latex nanocomposites depends on the nature of the silicates (layered or non-layered). It is found that viscosity decreases with shear rate for all silicates, and layered silicates register the higher shear viscosity values. The higher viscosity of layered silicate nanocomposites is due to the intercalation/exfoliation of rubber hydrocarbons. Natural rubber latex nanocomposites show shear thinning behaviour at higher shear rates owing to orientation of the exfoliated or intercalated structure along the shear direction. As the loading of layered silicate increases, the viscosity of the compound also increases, especially at low shear rates. From these rheological studies, the behaviour of latices modified with layered silicates can be understood. The intercalation/exfoliation can be related to the higher zero shear viscosity, higher yield stress, higher activation energy (E_a), and higher pseudoplasticity index (n).

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