Sulphur Prevulcanized Natural Rubber Latex-Based Nanocomposites with Layered Silicates

Sulphur prevulcanized natural rubber latex (PVNRL) nanocomposite was produced by mixing dispersions of layered silicates with prevulcanized latex. In this chapter layered silicates such as bentonite (natural) and flurohectorite (synthetic) were used in addition to a nonlayered amorphous filler (English Indian clay) as reference material. After compounding the layered silicate dispersions with PVNRL, films were prepared by casting. The post-vulcanized films of PVNRL nanocomposites were subjected to mechanical, swelling, XRD and TEM studies. In all respects layered silicate nanocomposites registered maximum properties compared to the reference material. This was explained to be due to the intercalation/exfoliation of the silicate layers by the natural rubber. It was found that the fine silicate layers form a skeleton network structure (house of cards) in the vulcanizate.

Part of this chapter was published in *J. Rubb. Res.*, 8(1), 1–15, 2005
3.1 Introduction

Vulcanized rubbers are usually reinforced by carbon black and also by inorganic minerals (talc, TiO$_2$, silicates etc) to improve the mechanical properties. Carbon black has an 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. Now-a-days there is a great interest in the development of polymeric nano-composites using layered silicates as reinforcing material [1-6]. Provided that the layered silicates fully delaminate (termed exfoliation) dispersing less than 10 percent 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 is credited to researchers at Toyota Central Research Laboratories (Japan): it became very popular in late1980s, which has been well reviewed [6-7]. Polymer nanocomposites represent a new alternative to conventionally (macroscopically) filled polymers. Because of their nanometer level 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 [7-10].

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 to 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 polymerization 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 200-300 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, research succeeded in intercalating many kinds of polymers and to prepare clay/polymer nanocomposites [13-17]. It has been shown that the silicate layers can be dispersed at molecular level (nanometer scale) in a polymer matrix [8]. 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 chapter natural (NR) latex
in the prevulcanized form was used to prepare nanocomposites. Properties of the nanocomposites were compared with vulcanizates containing an inert filler called English Indian clay (commercial or non-layered silicate).

### 3.2 Results and discussion

#### 3.2.1 XRD analysis

The XRD spectrum of the layered silicates showing the interplanar distances is given in Figure 3.1. The XRD spectrum of fluorohectorite showed 3 peaks, which from left correspond to an interlayer distances of 1.35, 1.24 and 1.05 nm respectively. The strong peak at 1.24 nm showed that majority of the layers in fluorohectorite have an interlayer distance of 1.24 nm.

![Figure 3.1 XRD of layered silicates (bentonite and fluorohectorite) and the non-layered silicate material (English Indian clay).](image)

The bentonite showed one peak which corresponds to an interlayer distance of 1.35 nm. The commercial clay has one narrow peak at 0.96 nm, which is not at all ideal for polymer intercalation.

3.2.2 TEM analysis

It will be interesting now to analyze the transmission electron microscopic (TEM) pictures of the composites. All the composites are loaded with 10 phr filler. In Figure 3.2a, the TEM picture of commercial clay (English Indian clay) loaded vulcanizate is given.

Figure 3. 2a TEM picture of commercial clay (English Indian clay) loaded vulcanizate

Here the filler exist as large particles and the bulk of the polymer did not contain any filler particle for reinforcement. 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 weaken the matrix. Recall that this clay was not a layered version.

Figure 3.2b TEM pictures of bentonite filled (nano)composites.

However in bentonite filled vulcanizate (Figure 3.2b), the filler exist as a network structure around the rubber particles (white portion). This is because the bentonite clay underwent some level of intercalation, and the silicate layers form ‘clusters or house of cards structure’. The high compound viscosity, which have 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 high mechanical properties of the vulcanizate.
However a fully saturated structure was observed in the case of fluorohectorite filled vulcanizate Figure 3.2c). Here, the silicate layers were intercalated to a great extent and a small level of exfoliation was also observed which exist 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 vulcanizate compared to that of bentonite. Moreover the exfoliated structure gives a several fold increase in surface area.

Figure 3. 2c TEM pictures of fluorohectorite filled (nano)composites

3.2.3 Mechanical properties

Figures 3.3a, b and c show the modulus at various elongations for different silicate filled vulcanizates Figure 3.3a illustrates the results of 3 phr
loaded vulcanizate. 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 < flurohectorite. As the elongation is increased the modulus also increased which is maximum at 300% elongation. It is to be noted that the maximum increase in modulus is with flurohectorite at 300% elongation followed by bentonite.

![Graph showing modulus change with various silicates at 5phr loading. Here also the change in modulus at various elongations is of the same order as we have discussed earlier. However at same elongation the magnitude of the modulus at 5 phr loading is higher when compared to that at 3phr loading (Figure 3.3a) especially with layered silicates. In the case of gum and commercial clay filled vulcanizates this difference](image)

**Figure 3.3a** Moduli at different elongations for different silicates filled (nano)composites at a loading of 3 phr

**Figure 3.3b** represents the modulus change with various silicates at 5phr loading. Here also the change in modulus at various elongations is of the same order as we have discussed earlier. However at same elongation the magnitude of the modulus at 5 phr loading is higher when compared to that at 3phr loading (Figure 3.3a) especially with layered silicates. In the case of gum and commercial clay filled vulcanizates this difference
is negligible. The silicate layers may favour the formation of immobilized or partially immobilized polymer phases, which may contribute for high modulus [17]. 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 vulcanizate containing layered silicate, a part of the silicate were exfoliated which offers high surface area for reinforcement. When the silicate loading is increased to 10phr (Figure 3.3c) layered silicates showed comparatively high modulus.

![Figure 3. 3b Moduli at different elongations for different silicates filled (nano) composites at a loading of 5phr](image-url)
Figure 3.3c Moduli at different elongations for different silicates filled (nano)composites at a loading of 10phr.

Figure 3.4 Tensile strength of different silicates filled (nano)composites at different loading
The effect of filler loading on tensile strength of the composites is shown in (Figure 3.4) which was found to increase up to 5 phr 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 phr.

Tear strength values of the composite are given in (Table 3.1). Addition of small amount of layered silicate (3phr) increased the tear strength considerably. It has been reported that exfoliated layered silicates can increase the tear strength considerably [17].

**Table 3.1** Tear strength of layered silicate filled vulcanizates

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Loading, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Flurohectorite, kN/m</td>
<td>47.98</td>
</tr>
<tr>
<td>Bentonite, kN/m</td>
<td>47.98</td>
</tr>
<tr>
<td>English Indian clay, kN/m</td>
<td>47.98</td>
</tr>
</tbody>
</table>

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 which results in high tear strength value in flurohectorite and bentonite. At high loading (above 5phr) the silicate layers agglomerate and exist as stacks, which can not orient in the strain direction. In the case of tear strength, the threshold level of silicate (layered) loading was observed to be 3phr.
The rate of relaxation of the composites with stress was fast in the case of layered silicate (Figure 3.5) incorporated vulcanizates and it is in the order flurohectorite > bentonite > commercial clay. At high elongation the chain slip along the filler surface is the major factor, which contribute to the stress decay and is proportional to the surface area of the filler in contact with the polymer. As the extend of exfoliation was high in flurohectorite, the surface area and hence the stress decay at a given elongation was proportionately higher in flurohectorite.

**Table 3.2 Tension set (%) of layered silicate filled vulcanizates.**

<table>
<thead>
<tr>
<th>Silicate</th>
<th>Loading, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Flurohectorite</td>
<td>2</td>
</tr>
<tr>
<td>Bentonite</td>
<td>2</td>
</tr>
<tr>
<td>English Indian clay</td>
<td>2</td>
</tr>
</tbody>
</table>
Tension set of the composites was determined and is given in (Table 3.2). Set was maximum with flurohectorite, 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 < flurohectorite.

### 3.2.4 Sorption behaviour

Table 3.3 shows the weight in grams of toluene absorbed per gram of the composite at 25°C. The gum vulcanizate has the maximum toluene uptake at equilibrium swelling.

<table>
<thead>
<tr>
<th>Loading, phr</th>
<th>0</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flurohectorite</td>
<td>4.93</td>
<td>4.74</td>
<td>4.49</td>
<td>4.312</td>
</tr>
<tr>
<td>Bentonite</td>
<td>4.93</td>
<td>4.85</td>
<td>4.6</td>
<td>4.35</td>
</tr>
<tr>
<td>English Indian clay</td>
<td>4.93</td>
<td>4.89</td>
<td>4.83</td>
<td>4.73</td>
</tr>
</tbody>
</table>

This was expected, since there was 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 with flurohectorite - compared to that containing commercial clay. During swelling the solvent can enter in the polymer along or transverse to the aligned silicate platelets. The presence of impermeable clay layers decreases the rate of transport by increasing the average diffusion path length in the specimen [18-19]. In commercial clay filled rubber, the solvent uptake is high 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, which show the ratio of the crosslink-density of the unfilled material (gum sample) to that of the filled vulcanizate are given Figure 3.6.

If the value $V_{r0}/V_{rf}$ is less than unity the filler rubber interactions are more and vice versa. It is interesting to note that for layered silicates $V_{r0}/V_{rf}$ is always less than one and the magnitude of the ratio decreases with filler loading. However in the case of English Indian clay the $V_{r0}/V_{rf}$ is always higher than 1 hence these composites showed low reinforcement and poor mechanical properties.

![Figure 3.6. Plots of $V_{r0}/V_{rf}$ against volume fraction of filler for different silicates-filled (nano) composites.](image-url)
3.3 Conclusion

Nanocomposites based on sulphur prevulcanized natural rubber latex and layered silicates were prepared. The vulcanized nanocomposite was subjected to mechanical analysis. It is found that the modulus and tear strength of the vulcanizate increases with the incorporation of layered silicate and in the case of layered silicates 3phr loading was found to be the threshold level for most of the mechanical properties. Higher loading leads to agglomeration or filler networking 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 is comparably better compared to the reference. The filler-rubber interactions are strong in layered silicate incorporated vulcanizate as evident from Kraus plots.

3.4 References


6. A. Usuki, A. Tukigase, M. Kato, Polymer, 43, 2185 - 2189, 2002


