Use of crystal violet to prepare SBR-montmorillonite clay nanocomposites

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Abstract: Present study describes the preparation and characterization of crystal violet modified-montmorillonite clay nanocomposites by latex blending technique. Coagulation of the latex-clay slurry produced nanocomposites master batch. The master batch was compounded with Styrene Butadiene rubber (SBR). WAXD and TEM provided the evidences of formation of nanocomposite. Remarkable improvements in the mechanical properties were found by addition of small amount of modified clay.

Key words: Nanocomposites, Crystal Violet, Montmorillonite clay, SBR rubber.

Introduction

Till date, research involving layered silicates of synthetic and natural origin for the property modification of polymers was mostly devoted to thermoplastics [1-6] and thermosetting resins [1,2,7,8]. However, elastomers and rubbers are very promising polymeric matrices for the preparation of polymer clay nanocomposites (PCN) due to the following reasons [9]:

(i) It is well known that amine compounds act as curing reaction activators in sulfur containing rubber recipes [10]. Thus, PCNs intercalated by amine compounds may interact with the sulfur curatives thereby promoting thermodynamically favored interactions between the rubber chains and the silicate layers leading to increased intercalation/exfoliation.

(ii) Rubbers exhibit high melt viscosities during melt mixing due to their high molecular weight and this paves the path for generation of high shear stresses for the shearing and peeling apart of the silicate layers.

(iii) Further, the swelling of pristine and organophilic clays in both aqueous and organic solutions makes it amenable for the preparation of rubber clay nanocomposites via the latex and solution routes.

PCNs are currently prepared either by solution blending, or by latex compounding, or by direct intercalation of the molten polymer (melt intercalation), or by sol/gel technology, or by in-situ polymerization.
Most of the rubbers are available in the form of latex which is nothing but an aqueous dispersion of rubber particles in the submicron-micron range (the particle size distribution depending on the manufacturing conditions). The layered silicates are easily dispersed in water as water acts as a swelling agent owing to the hydration of the intergallery cations usually Na\(^+\) or K\(^+\). The water swelling capability of the natural clays are not the same but depend upon the type of clay and its cation exchange capacity [11] and hence the mixing of the latex with the layered silicates (having high cation exchange capacity) followed by co-precipitation (coagulation) is a promising route for producing rubber nanocomposites [9].

Varghese and Karger-Kocsis prepared NR based nanocomposites with 10 wt% natural (sodium bentonite) and synthetic (sodium fluorohectorite) layered silicates by the latex compounding method [12]. Wang et al. prepared NR-MMT and chloroprene rubber (CR)-MMT clay nanocomposites by co-coagulating the rubber latex and the aqueous clay suspension [13]. Stephen et al. studied the impact of layered silicates like sodium bentonite and sodium fluorohectorite on the rheological behavior of NR, carboxylated SBR (XSBR) latices and their blends with special reference to shear rate, temperature and filler loading [14]. Zhang et al. prepared clay (natural clay fractionated from bentonite)-SBR nanocomposites by mixing the SBR latex with a clay/water dispersion and coagulating the mixture [15]. Zhang et al. investigated the flammability of MMT/SBR nanocomposites prepared by the technique of co-coagulating rubber latex and clay aqueous dispersion [16].

In the present study, authors have used crystal violet for the preparation of the nanocomposites. Crystal violet or Gentian violet (also hexamethyl pararosaniline chloride) is a triarylmethane dye. The dye is used as a histological stain and in Gram’s method of classifying bacteria. It is also known as Methyl Violet 10B.

**Results and discussion**

**WAXD study**

Figure 1 shows the X-ray diffraction patterns of Kunipia F clay, modified clay master batch, compound A & B respectively. Kunipia F shows a characteristic diffraction peak at 2\(\theta\) ~ 7.24 ° corresponding to an inter-gallery distance of 1.22 nm. The clay present in the modified clay master exhibited a characteristic diffraction peak at 2\(\theta\) ~ 4.9 ° corresponding to an inter-gallery distance of 1.80 nm. In case of compound B, a peak at 4.6 ° corresponding to a layer spacing of 1.92 nm was generated. The intercalation of the polymer and partial exfoliation of the clay layers led to disordering of the layered clay structure causing the decrease in the XRD coherent layer scattering intensity of compound B. This is clearly indicating that the crystal violet acts as an effective intercalate. However, compound A did not exhibit any shift in the diffraction peak and thus the inter-gallery distance in compound A remained the same as in case of Kunipia F clay.

During compounding mixing, the diffraction peak was shifted from 1.80 nm (in the master batch) to 1.92 nm in the compound B. The shearing force generated during mixing probably further helped the clay to disperse in to the matrix.

**TEM study**

TEM was used to visualize the morphology of the clay layers, stacks and aggregates in the nanocomposites.
**Fig. 1.** X ray diffractogram of compound A, B Kunipia clay & modified clay master batch.

**Fig. 2.** TEM image of compounds (Figure A, B – compound B, Figure C,D- compound C, Figure E - compound A).
Figure 2 shows TEM micrographs for samples with 5 & 10 phr of modified clay. Even though XRD indicated primarily intercalated structures, different populations of exfoliated nanolayers, stacks of nanolayers and clay tactoids were revealed by TEM for compound B (Figure 4, A & B) and C (Figure 4, C & D) respectively. The dark lines in the TEM micrograph (compound B, Figure 4, A & B) correspond to the clay nanolayers. The aggregates are homogeneously dispersed. The thinner aggregates correspond to fewer nanolayers in the stacks (thickness ~ 10-15 nm). The thicker aggregates correspond to the thickness of ~ 30-40 nm. Similar observations were made at higher concentrations of clay in compound C (Figure 4, C & D). However, in compound A, a large number of undispersed particles in the range of 500-1000 nm were observed. Thus crystal violet helped to achieve partially exfoliated and intercalated nanocomposites.

Fig. 3. TGA thermogram of the compounds.

Fig. 4. DTGA thermogram of the compounds.
**TGA study**

The TGA and DTG curves of the compound A, B and C are compared in Figure 3 & 4, while the decomposition up to 450 °C, the peak decomposition temperatures and the corresponding peak decomposition rates for the compounds are tabulated in Table 1.

**Tab. 1.** Thermal characteristics of the compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decomposition up to 450 °C (%)</th>
<th>Peak decomposition temperature (°C)</th>
<th>Peak decomposition rate (%/min)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40.0</td>
<td>473</td>
<td>-45.0</td>
<td>-54.0</td>
</tr>
<tr>
<td>B</td>
<td>30.0</td>
<td>475</td>
<td>-42.0</td>
<td>-49.0</td>
</tr>
<tr>
<td>C</td>
<td>23.0</td>
<td>495</td>
<td>-40.0</td>
<td>-45.0</td>
</tr>
</tbody>
</table>

The decomposition amount up to 450 °C was around ~ 40% in case of compound A compared to that of ~ 30% and 23% for compound B & C respectively. The peak decomposition temperature followed the trend A<B<C and exact reverse trend was followed for the peak decomposition rate. Compound A was conventional macro composite with 5 phr of Kunipia clay. As a result, the thermal stability was very low. The thermal stability of compound B and C was much better in comparison to compound A. This was due to nano scale dispersion of clay in the matrix of compound B and C. Compound C had 5 phr of nano clay where as compound C had 10 phr. Thus, the thermal stability of compound C was higher in comparison to compound B. The better thermal stability can be attributed to the carbonaceous char formed and the structure of the clay minerals. The multiplayer clay structure acts as an excellent insulator and barrier for the mass transfer.

**Fig. 5.** DSC thermogram of the compounds.
**DSC study**

Dynamic DSC scans for the samples are shown in Figure 5. The glass transition ($T_g$) temperature of compound A was observed at ~ -55 °C while Compound B and C exhibited $T_g$s at ~ -49.0 & -45.0 °C respectively. These peak shifts can be explained on the basis of restricted mobility of the SBR chains within the clay layers thereby proving the intercalated / exfoliated nature of the SBR / crystal violet modified Kunipia F clay nanocomposites [17]. Thus in case of compound B and C, effective intercalation and/or exfoliation of the of the clay has increased the $T_g$. At higher clay loading (compound C), the $T_g$ shift was higher. The DSC findings are represented in Table 1.

**Rheometric property of the compounds**

The rheometric properties of the compounds are compiled in Table 2. The extent of curing (given by the $\Delta$Torque values) is highest in compound C followed by compound B and A respectively. This may be explained due to presence of organo clay in compounds B and C. The effective intercalation of the SBR rubber chains into the galleries of the clay resulting in higher rubber-to-filler interaction in the corresponding compounds which in turn gave raise higher torque. Compound A is a conventional composite. There was no such reinforcing effect from clay. As a result, the extent of curing was lowest in compound A. The cure rate index (CRI, rate of curing reaction) followed the same trend. Compound C exhibited height cure rate index of 18.5. It seems that the organo clay act as an effective vulcanizing agent. The crystal violet (more precisely the amine moiety of the crystal violet) present within the nanosilicate layer of the clay facilitates the vulcanization reaction. It has been reported that the amine moiety accelerate the curing reaction [17]. In compound C, availability of the crystal violet was highest. This give rise to the highest CRI value for compound C in comparison to compound B. The amine moiety of the crystal violet acts as a secondary accelerator for the curing reaction. In compound A, there was no such activation. As a result, the CRI was lowest for compound A. $t_{s2}$ (cure safety time, time require to increase the torque by two units from minimum torque value) and $t_{c90}$ (time require to teach the 90% of the maximum torque value) also followed the same trend.

**Tab. 2.** Rheometric property.

<table>
<thead>
<tr>
<th>Property</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Torque ($T_{\text{max}}$), (dN-m)</td>
<td>6.3</td>
<td>10.7</td>
<td>11.5</td>
</tr>
<tr>
<td>Minimum Torque ($T_{\text{min}}$), (dN-m)</td>
<td>1.6</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>$\Delta$Torque = $T_{\text{max}} - T_{\text{min}}$, (dN-m)</td>
<td>4.7</td>
<td>9.2</td>
<td>9.9</td>
</tr>
<tr>
<td>Scorch time ,$t_{s2}$ (min)</td>
<td>13.3</td>
<td>1.6</td>
<td>1.1</td>
</tr>
<tr>
<td>$t_{c90}$ (min)</td>
<td>24.3</td>
<td>7.9</td>
<td>6.5</td>
</tr>
<tr>
<td>Cure rate index, CRI (min$^{-1}$)</td>
<td>9.1</td>
<td>15.9</td>
<td>18.5</td>
</tr>
</tbody>
</table>
Physical property of the compounds

The physical properties of the compounds are compared in Table 3. The mechanical properties, viz., 50 and 300 % modulus, tensile strength and tear strength was maximum in compound C followed by compound B and A respectively. The addition of 5 phr of crystal violet modified clay results in an increase of ~ 50 %, 105 % and 60% in the unaged 50%, 300 % and tensile strength respectively but a nominal increase of ~ 6 % in the unaged elongation at break (EB) over regular compound A.

Tab. 3. Physical properties of compound A, B & C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%mod(MPa)</td>
<td>0.6</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>300%mod(MPa)</td>
<td>2.0</td>
<td>4.1</td>
<td>7.4</td>
</tr>
<tr>
<td>TS(MPa)</td>
<td>3.0</td>
<td>4.8</td>
<td>8.2</td>
</tr>
<tr>
<td>EB (%)</td>
<td>351</td>
<td>371</td>
<td>396</td>
</tr>
<tr>
<td>Hard ness (S)</td>
<td>45</td>
<td>52</td>
<td>58</td>
</tr>
<tr>
<td>Swelling index</td>
<td>5.72</td>
<td>3.85</td>
<td>3.65</td>
</tr>
<tr>
<td>Volume fraction (Vr)</td>
<td>0.140</td>
<td>0.182</td>
<td>0.211</td>
</tr>
<tr>
<td>Tear (N/mm)</td>
<td>17.88</td>
<td>26.7</td>
<td>34.0</td>
</tr>
<tr>
<td>Bound rubber (%)</td>
<td>13.0</td>
<td>23.5</td>
<td>27.9</td>
</tr>
<tr>
<td>Mooney ML (1+4) @ 100 C</td>
<td>47.2</td>
<td>66.9</td>
<td>70.6</td>
</tr>
<tr>
<td>Rebound resilience</td>
<td>62.0</td>
<td>64.8</td>
<td>64.4</td>
</tr>
<tr>
<td>Compression set @ 105 C / 24 hr (%)</td>
<td>37</td>
<td>39.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Air permeability</td>
<td>2.35</td>
<td>2.0</td>
<td>1.68</td>
</tr>
</tbody>
</table>

(The tensile properties of the compounds are the mean of five measurements and the rest properties are the mean of two observations)

Further, when 10 phr of crystal violet modified clay was added as in compound C, the corresponding increases in the unaged 50% modulus, 300% modulus, tensile strength and EB break are ~ 115, 320, 170% and 13 %, respectively over compound A. The intercalation and/or exfoliation of the SBR chains in the crystal violet-modified clay are probably responsible for the increase in tensile properties. Both A and B contain the same phr of clay filler but the sole difference between them is that Kunipia clay was crystal violet-modified in B and as a result the corresponding increase in the unaged 50 % modulus, 300 % modulus, tensile strength and EB over compound A. The TEM micrograph (Figure 2) corroborates the partial exfoliation and
intercalation of the clay platelets in B and C and this is responsible for the increase in mechanical properties.

Hardness of compound B and C was also higher in comparison to compound A. It is observed that the hardness increases with loading which is obvious from the fact that with increase in filler loading the modulus increases and hardness being a surface property also reflects a similar trend. However, the dispersion of the filler in the polymer matrix is also important and that is why compound A shows a lower Shore A hardness than B or C.

In compound B and C, swelling index decreases with increase in clay loading and this is due to intercalation and / or partial exfoliation of the SBR chains in the gallery gap of the bentonite clay. Exact reverse trend was found in volume fraction measurement. However, the crystal violet -modified clay paves the way for the entry of the SBR chains resulting in intercalation and / or exfoliation and this result in lower swelling tendency of the SBR chains. The rubber-filler interactions as measured by the bound rubber indicating the same fact. The higher the bound rubber, the higher is the polymer-filler interaction [18]. The bound rubber increases from compound A to C. Due to the same reason, the Mooney viscosity of compound C is higher compared to compounds B & A.

![Structure of crystal violet.](image)

With increase in modified clay content, the rebound resilience decreases and compression set increases. This was probably due to irreversible slippage of the rubber chain from the clay surface. It has been reported that the compression set [18] and rebound property [19] decreases in presence of organo clay. Rebound resilience is lowest in compound C followed by compound B, and A respectively. The compression set of compound C is also highest. Air permeability was found to be lowest in compound C followed by compound B, and A.

**Conclusions**

The above study indicated that the crystal violet can be used successfully to produce the nanocomposites. The structure of crystal violet is given in Figure 6. When dissolved in water, it forms hexamethyl pararosanilinium ion, which undergoes cation exchange reaction with the sodium ion of the montmorillonite clay. The mixing of the crystal violet modified clay master batch with rubber generated intercalated and
partially exfoliated nanocomposite. The fact is confirmed by the huge improvement in the physical property.

**Experimental part**

**Materials**

The SBR latex (Encord 205) with 25% bound styrene and 40% solids content was supplied by M/S Jubilant Organosys, Borada India. The Mooney viscosity (ML [1+4] at 100 °C) of the coagulated SBR latex was 51. Apart from SBR latex, SBR 1502 (emulsion grade) from BST Elastomers, Bankok Thailand (bound styrene 24 %, Mooney viscosity 50 (ML [1+4] at 100 °C), volatile matter 0.02 %, specific gravity 0.94) was also used in the compound formulations. Unpublished work in our laboratory indicates that the gum properties of both those SBRs are similar and thus SBR 1502 was used for dose adjustment during compound formulation as reported later.

Sodium montmorillonite clay (Kunipia F) was obtained from Kunimin Industries Co. Ltd, Japan (CEC 115 meq/100 g).

The rubber compounding ingredients used in this work were of commercial grade, viz. zinc oxide, stearic acid, sulfur and N-t-butylbenzothiazole-2-sulphenamide (TBBS). Crystal Violet was purchased from Qualigens, Mimbai, India.

**Synthesis of the crystal violet modified montmorillonite clay nanocomposite master batch**

About 10 gm of kunipia F was vigorously stirred (at 1500-200 rpm) in 700 ml of water at 80 °C. Stirring was continued for 2 hr. About 7.34 gm (~ 1.5 times of the CEC of the clay) of crystal violet was dissolve in 500 ml of distilled water with stirring till complete dissolution. The crystal violet solution was added in to the clay slurry. The mixture was further stirred (at 1500-2000 rpm) at 80 °C for 2 hr. Diluted SBR latex (40% total solid) was then added to the aqueous slurry. At this stage, heating was discontinued. The latex–clay slurry was stirred (at 1500-2000 rpm) for another 1 hr. The amount of latex was adjusted to make 30 parts of clay in 100 parts of rubber (i.e. 30 phr weight parts of clay per hundred weight parts of rubber) on dry basis. The resultant solution was coagulated with diluted sulfuric acid. The mass was washed several times with tap water and dried at 70 °C or below in a hot air oven. The stirred used in this study was from REMI (Model RQ 124A). The mixer shaft length & dia was 8 X 300 mm. The impeller was pitched fan type.

**Compound mixing**

The single stage mixing was done in a Brabender Plasticorder model PL 2000-3 (Brabender, Germany) having a chamber volume of 80 cm³, cam rotors, ram pressure weight of 5 kg and batch weight of 70 g. Single stage mixing was carried out for 10 minutes using 60 rpm rotor speed at 70 °C. Initially 1 min mastication time was allowed for the rubber. Then clay or clay master batch was added and mixed for 6 minutes. Then, the other ingredients were added and the batch dumped after 3 minutes.

The mixed batches were further milled on a laboratory two-roll mill from Santosh Industries, Mumbai, India. The compound formulation is shown in Table 4.
**Tab. 4.** Formulation of the compounds.

<table>
<thead>
<tr>
<th>Material (phr, parts per 100 parts of rubber)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene butadiene rubber (SBR1502)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide (ZnO)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TBBS</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>Clay from insitu crystal violet-modified master batch</td>
<td>-</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Clay from latex-clay master batch, without crystal violet treatment</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In compound A, clay was added from the clay-latex master batch (without crystal violet treatment) and thus can be taken as regular compound. Both compound B and C contain crystal violet modified clay added from crystal violet treated clay –latex master batch. The SBR dose was adjusted by adding SBR 1502 during mixing.

**Characterization of the SBR / clay nanocomposites**

Wide angle X-ray diffraction (WAXD) measurements were carried out in a Philips 1710 X-ray diffractometer using a scan rate of 0.5°/min with Cu Kα target at 40 kV and 25 mA (wavelength = 0.154 nm) with 20 scan range from ~ 2 to 10°. The XRD diffractogram is presented in Figure 1.

For transmission electron microscopy (TEM) measurements, 100 nm sections were microtomed at -120 °C using Ultracut E ultra microtome (Reichert and Jung) with a diamond knife. Measurements were carried out with a Philips CM200 TEM at an acceleration voltage of 120 kV. The TEM micrographs are given in Figure 2.

The thermal stability of the cured samples was determined from the TGA study using Pyris-1 TGA of M/s Perkin Elmer, Shelton, USA. Initially the sample was heated under nitrogen atmosphere up to 600 °C and then the gas was changed to oxygen and the heating continued up to 800 °C. The heating rate was 40 °C/min. For each sample three tests were carried out under the same heating rate and the temperatures were reproducible to ± 3.0 °C. Summarized results are reported in Table 1. The TGA and DTGA thermograms are shown in Figure 3 & 4 respectively.

Differential scanning calorimetry (DSC) experiments were performed in dynamic mode using Diamond DSC (Perkin Elmer, Norwalk, USA) to measure the glass transition temperature (T_g). The scans were carried out from −100 to 20 °C at a heating rate of 20 °C / min under nitrogen atmosphere. The findings are shown in Figure 5.
The rheometric properties were determined in a moving die rheometer (MDR 2000E) from M/s Alpha Technologies, Akron, USA at 160 °C for 30 minutes keeping the rotor arc at 0.5° in accordance with ASTM D 5289. Rheometric properties are reported in Table 2.

Curing of tensile slabs was done using a compression molding technique in an electrically heated curing press from M/s Hind Hydraulics, New Delhi, India at 160 °C for 30 minutes. The tensile samples were died out in accordance with ASTM D412 type C die.

The stress – strain properties were determined using a universal testing machine, Zwick UTM 1445 from M/s Zwick, Ulm, Germany in accordance with ASTM D412. The hardness was determined in a Shore A durometer from M/s Prolific Industries, New Delhi, India in accordance with ASTM D2240.

The tear properties were measured according to ASTM D624. The Mooney viscosity was measured using MV2000E from Alfa Technologies, Akron, USA in accordance with ISO 289-1.

Cure rate index (CRI) was measured according to ASTM D5289. The following formula was used for the CRI in the study:

\[
\text{CRI} = \frac{100}{t_{c90} - t_{s2}}
\]  
where ,

The swelling index of the cured samples was measured using the following formula in accordance with ASTM D3616:

\[
\text{Swelling Index} = \frac{\text{S weight}}{\text{Initial weight}}
\]

Volume fraction was also performed to get an indication of apparent crosslink density. Weighed sample of cured rubber vulcanizate was immersed in toluene solvent for 48 hrs at room temperature. Excess solvent was then blotted from the sample and the swollen weight was measured. The swollen sample was dried in oven at 100 °C till constant weight. Dried weight of the sample was taken after cooling the sample in the desiccator. The volume fraction, \(V_r\) of the vulcanizate rubber was calculated using following formula:

\[
V_r = \frac{(D - FT) / \rho_r}{(D - FT) / \rho_r + A_0 / \rho_s}
\]

where \(D\) is the weight of the deswollen sample; \(F\) is the weight fraction of the insoluble non-rubber ingredients; \(T\) is the original dry weight of the sample; \(A_0\) is the weight of solvent absorbed; \(\rho_r\) is the density of the rubber (density value of SBR rubber is 910 kg/m³); and \(\rho_s\) is the density of the solvent (density value of toluene is 870 kg/m³).

Bound rubber content was also measured by using the following formula:

\[
\text{Bound rubber} = \frac{(M_B - M_F - M_D)}{M_B} \times 100\%
\]
where \( M_B \) = Weight of the uncured mix before immersing, \( M_F \) = Weight of the filler in the uncured mix and \( M_D \) = Weight of the rubber dissolve in the solvent.

Rebound resilience and compression set of samples were carried out according to ISO 4662 and ASTM D395 respectively. Air permeability test was carried out according to ISO 2782.

The physical properties are summarized in Table 3.

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**References**


