8.1 Introduction

The use of different types of nanofillers in the preparation of polymer nanocomposites (PNC) is emerging as a new class of industrially important material. Of particular interest is the recently developed nanocomposites containing polymer and a layered silicate. Polymer/layered silicate nanocomposite often exhibit remarkable improvement in properties when compared to virgin polymer or conventional micro and macro composites [1].
The most commonly used layered silicates are montmorillonite, hectorite and saponite \([2,3]\) having different chemical formula.

- **Montmorillonite**: \(Mx(Al_{4-x}Mg)Si_8O_{20}(OH)_4\)
- **Hectorite**: \(Mx(Mg_{6-x}Li)xSi_8O_{20}(OH)_4\)
- **Saponite**: \(MxMg_6(Si_{8-x}Al)xO_{20}(OH)_4\)

These materials are found abundantly in nature, but are contaminated with impurities. They are usually synthesised in the pure form under hydrothermal conditions \([4,5]\). Hydrothermal method involves conventional heating with agitation under reflux at atmospheric pressure or heating at high temperature and pressure. This is a time consuming process and requires specialized and costly equipments for the reaction to take place. Moreover the method has the disadvantage of non uniform heating. The surfaces, edges and corners of the particles are heated more than the inside of the material.

The major advantages of this method are uniform heating, reduction in heating time, reduction in capital and operating costs. Further the silicates are obtained in a substantially pure form, so that further purification process can be avoided.

The starting materials usually used in the preparation of layered silicates include silica sources like silica gel, silica powder and colloidal silica. The cheapest raw material among the silica sources is sodium silicate solution.

In this work layered silicates were prepared by microwave heating technique. Three metal chlorides of Mg, Li and Al were primarily selected.
for the synthesis of layered silicates. A combination of magnesium and aluminium metal chlorides selected for synthesis of layered silicate was designated as LS1 and the layered silicate designated as LS2 was prepared by replacing aluminium chloride with lithium chloride. Further the layered silicate, LS2 was modified after synthesis, with CTAB and it was designated as MLS2.

8.2 Experimental

8.2.1 Materials

Lithium chloride (AR), Aluminium chloride (AR), Magnesium chloride (AR) and CTAB (Hexadecyl triethyl ammonium bromide) were purchased from Alpha Chemicals, Ernakulam

Sodium silicate was purchased from Minar Chemicals, Edayar, Cochin.

All other chemicals were of commercial grade.

8.2.2 Methods Used

8.2.2.1 Preparation of layered silicate (1): LS1

To an aqueous solution of sodium silicate (60%), HNO3 was added dropwise, followed by a well stirred mixture of MgCl2 (71.1g) and AlCl3 (5.66g). To the thus obtained silicicacid-magnesium-aluminium aqueous solution 2N NaOH solution was added over a period of 5 minutes with vigorous agitation until pH=10. The precipitate formed was immediately removed by filtration and after repeated washing with water, 1N NaOH was added and the pH of the slurry was made to 11.6. It was then heated in a microwave oven at a frequency 2450 MHz for 40 minutes. The resulting product was washed with water, dried at room temperature and very finely powdered [6, 7]
8.2.2.2 Preparation of layered silicate (2):LS2

69g MgCl₂ (99% purity) and 2.12g LiCl (99% purity) were homogeneously stirred in 500 ml water and added dropwise to a 60% sodium silicate solution. The solution was continuously stirred for 2 hrs. 0.1 M NaOH was added dropwise to the above solution to raise the pH to 9.5 [4, 8, 9]. After vigorous stirring the mixture was kept in a microwave oven with operating frequency 2450 MHz for 40 minutes. The product obtained was washed with water, filtered and dried at 250°C for 8hrs.

8.2.2.3 Modification of Layered silicate (2)

MgCl₂ and LiCl were added to Na₂SiO₃ solution as per the above discussed procedure. To this solution a mixture of 25% aqueous solution of CTAB and ethylene glycol were added under vigorous stirring at room temperature for 1hour. By adding NaOH, pH of the mixture was adjusted to 9.5. The mixture was kept in a microwave for 40 minutes. The product was washed with water, filtered and dried at 250°C for 8 hrs. Modified layered silicate thus obtained was designated as MLS2

Microwave heating of all the samples were done on a NG microwave appliance (Model number MS 1911HE) having a frequency 2450MHz (RS output 7000W, microwave 1000W).

8.2.3 Characterization

The silicates were characterized by XRD (2.4.10), FTIR (2.4.11), HRTEM (2.4.12), SEM (2.4.13), EDS (2.4.14) and ICPAES (2.4.15) analysis.
8.3 Results and Discussion

8.3.1 X-ray diffraction analysis (XRD)

X-ray diffraction pattern of layered silicate (LS1) is given in Fig. 8.1. The diffraction patterns were obtained at d spacing 2.51 Å and 1.54 Å corresponding to the 2θ value 35.63° and 60° respectively.

Fig. 8.2 shows the XRD pattern of the layered silicate (LS2). The measured diffraction peaks were at 2θ = 6.3° and 35.6° corresponding to an interlayer spacing of 13.91 Å and 2.52 Å respectively. Other peaks resulted from the multiple reflections as predicted by Bragg’s law. [10]. The typical pattern of a synthetic hectorite gave peaks at 14.3 Å (2θ = 6.18°) and 2.56 Å (2θ = 35.6°) for (001) and (130) reflection planes respectively [11, 12]. Thus the XRD interpretations confirmed that the structure of the prepared silicate resembled closely the hectorite class silicates. The miscellaneous peaks at 27° and 32° showed some deviation from definition. Particle size as calculated using Debye Scherrer equation.
was 36.1 nm. As evidenced from TEM pictures both silicates had particle size in the range of nanometers. Also the interlayer spacing which is the beneficial factor on which the performance of a silicate depends; increased for LS2, compared to LS1. Though both had a d-spacing of 2.5 Å, at 2θ = 35.6° the d-spacing was good with LS2 as indicated by the peak at 2θ = 6.3° with d=13.91Å

![Fig.8.2. X-ray diffraction pattern of layered silicate (LS2)](image)

Fig. 8.2. X-ray diffraction pattern of layered silicate (LS2)

Fig.8.3 shows the XRD pattern of the layered silicate LS2 modified with CTAB (MLS2).

On modification with CTAB, the peak at 6.3° was shifted to a lower angle 5.5° with an increase in the interlayer spacing (from 13.91Å to 16Å). The peak at 35.6° broadened and shifted slightly to the smaller angle. This broadening of the peak indicated that modification caused some degree of disorder of the crystallites. Thus the intercalation of CTAB into the gallery space was confirmed by this broadening characteristic observed in XRD. Helena Palkova et al. [13] exchanged sodium for HDTMA (hexa decyl tri
methyl ammonium) cations in Laponite (Laponite is a synthetic layered hydrous magnesium silicate resembling hectorite) and observed an expansion of clay layers with a shift in the basal reflection to lower 2θ value (estimated value is in the range 17-22 Å). Lagaly and Weiss had suggested that such a value points to the bilayer or pseudo tri molecular layer arrangement of surfactant cations in the inter gallery space [13].

![X-ray diffraction pattern of modified layered silicate (MLS2)](image)

**Fig. 8.3.** X-ray diffraction pattern of modified layered silicate (MLS2)

### 8.3.2 Fourier transform infrared spectroscopy (FTIR)

IR spectrum of the layered silicate (LS1) prepared by microwave heating is given in Fig. 8.4. The peaks at 3454 cm⁻¹ represents the stretching vibration of OH groups. The peak at 1017 cm⁻¹ was due to the adsorbed water molecules and the band at ~1644 cm⁻¹ represented the stretching of Si-O-R group.
Fig. 8.4. FTIR spectrum of layered silicate LS1

Fig. 8.5 is the IR spectrum of layered silicate (LS2). The presence of hydroxyl groups at 3445 cm$^{-1}$ might be formed by the overlapping of stretching vibrations due to Si-OH and Mg-OH groups [14]. Band at 1029 cm$^{-1}$ represents Si-O and Si-O-Si stretching vibration and the one at 666 cm$^{-1}$ resulted from the weak OH bending vibration from adsorbed water. Physically adsorbed water in the form of association of molecules gave an absorption band at 1639 cm$^{-1}$ [15, 16]. The IR spectrum obtained once again reminded us of a synthetic hectorite.

Fig. 8.5. FTIR spectrum of layered silicate LS2.
Modification of clay with CTAB introduced peaks at 2920 and 2855 cm$^{-1}$ corresponding to asymmetric and symmetric C-H stretch vibrations of the modifying group. Band at 1470 cm$^{-1}$ was assigned to the ammonium salt [17]. The relatively lower intensity of the band centered around 3440 cm$^{-1}$ and the deformation band at 1640 cm$^{-1}$ indicated a reduction in the adsorbed water content. These bands indicate that, modification made clay hydrophobic [16]. Fig. 8.6. is the IR spectrum of modified silicate MLS2

![FTIR spectrum of modified layered silicate MLS](image)

**Fig.8.6. FTIR spectrum of modified layered silicate MLS**

**8.3.3 Scanning electron microscopy (SEM)**

Fig.8.7 shows the SEM image of layered silicates LS1. A layer like structure was evident from the photograph. Fig.8.8 is the SEM image of LS2. The images clearly indicates the strong tendency of particles to form agglomerates of irregular shapes
8.3.4 Energy dispersive spectrometry (EDS)

The EDS spectra assisted to some extent the confirmation of compositional purity of silicates prepared. EDS of layered silicates given in Fig 8.9 and Fig 8.10 confirmed the presence of all the elements in the silicates LS1 and LS2. EDS of layered silicate LS1 (Fig 8.9) showed the presence of Na, Mg, Al, Si and O. Fig 8.10 is the EDS of layered silicate LS2. It gave the presence of Mg, Si, O and Na. The presence of Li cannot be detected by EDS, since the EDS source was based on Beryllium.
8.3.5 Inductively coupled plasma atomic emission spectrometry (ICP-AES)

Presence of Li in LS2, along with Mg and Na was further confirmed by ICPAES analysis. Table 8.1 gives the result of ICPAES analysis conducted on LS2.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Li6707</th>
<th>Mg 2852</th>
<th>Na 5889</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS2</td>
<td>17.6</td>
<td>0.054</td>
<td>1.365</td>
</tr>
</tbody>
</table>

8.3.6 High resolution transmission electron microscopy (HRTEM)

Fig.8.11 and Fig.8.12 shows the TEM images of the layered silicates (LS2) and modified layered silicate (MLS2). The dark areas were the aggregated silicate layers. From the lighter shades seen in the images it was clear that the particle sizes of both silicates were in the nanometer range. It appeared that modified silicate was fully enveloped by the surfactant CTAB.
8.4 Conclusions

Microwave technique proved to be an effective method for the production of layered silicates. The presence of lithium instead of aluminium affected the overall performance of the silicates. XRD analysis of LS2 was similar to that of hectorite. Modification of LS2 by CTAB was confirmed by IR analysis. XRD analysis of MLS2 showed an increase in interlayer spacing. SEM images of LS1 showed layered structure. TEM images of LS2 and MLS2 showed agglomeration of particles.
8.5 Introduction

Layered silicate based nanocomposites have received considerable interest recently, owing to the simple and cost effective method of enhancing polymer properties by the incorporation of fillers at the nanometer level. Naturally occurring layered silicates are usually impure and is undesirable in many industrial applications. Synthetic silicates on the other hand are considered environmentally benign, nanoparticulate material with unique electrical, mechanical and rheological properties, which are of interest to a number of industries [12.] Among the various types of layered silicates available, montmorillonite is the most widely studied [18, 19]

One of the main problems encountered in the preparation of polymer/layered silicate nanocomposite consists in providing complete delamination of the silicate layers and a uniform dispersion of the filler particles over the polymer matrix. Fischer et al. [20] have suggested that complete delamination is not a necessary condition for preparing nanocomposites with improved properties.

In this part the layered silicates LS1, LS2 and MLS2 were incorporated in XNBR /SBR latices as well as NBR / SBR dry rubber, to assess their reinforcing effect. The mechanical properties of the composites were studied.
8.6 Experimental

8.6.1 Materials

XNBR-Carboxylated NBR latex, CLX 530, was purchased from Eliokem India Pvt. Ltd. Bombay. Specification is given in Table 2.1.

SBR-Encord 204 latex is styrene butadiene copolymer latex, supplied by Jubilant Organosys Limited. Gujarat Specification is given in Table 2.2.

NBR-Nitrile rubber–KNB 35L with acrylonitrile content (% by weight) 34 and Mooney viscosity ML (1+4) at 100°C=41, supplied by Kumho Petrochemicals Co., Ltd.

SBR- Kumho SBR (SBR-1502) with bound styrene content 24 and Mooney viscosity ML (1+4) at 100°C= 56 was supplied by Kumho Petrochemicals Co., Ltd.

8.6.2 Preparation of composites

The silicates were finely powdered and 50% dispersions were made by ball milling for 24 hrs. The compounding ingredients were added to XNBR and SBR latices as per the formulation given in Table 3.3 and Table 3.4 respectively. 5phr each of the prepared silicates were added in XNBR and SBR. Composites were prepared according to the procedure given in section 3.11.1. NBR sheets were cured at 30 min (100°C) and SBR sheets were cured for 40 min (110°C).

Compounding of NBRand SBR (dry rubber) was done on a two roll mill (Section 3.11.4) according to the formulation given in Table 3.5 and Table 3.6. Mixing of NBR and SBR were done as per ASTM D 3187-001 and 3185-99 respectively. 5phr each of the prepared silicates were added in
Preparation of layered silicates, its characterization and use in XNBR/SBR lattices and NBR/SBR dry rubber.

NBR and SBR. The nip gap was set at 0.2 mm and temperature maintained a 50+/– 5°C. The mixed compounds were matured for a period of 24 hrs and cure characteristics were determined using rubber process analyzer (RPA 2000 Alpha Technologies, 2.4.3) at a temperature of 160°C.

8.6.3 Methods

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on an electrically heated press. Details of the process are given in Section 2.4.4.

Mechanical properties of the composites were studied as per ASTM D 412-2002 on a Shimadzu Model AGI Universal Testing Machine using test specimens punched out from the molded sheet using the C-type die. The measurements were carried out at a cross head speed of 500 mm/min.

8.7 Results and Discussion

8.7.1 Mechanical Properties

Fig.8.13.(A)-(D) shows the variation of tensile strength, elongation at break, modulus and tear strength of the silicates in the various elastomeric matrices. Of the three types of layered silicates prepared LS2 showed the maximum reinforcing effect. The layered silicate (LS2), must be a porous fibrous clay, like hecorite [10]. The nanosize of LS2 as determined by XRD and SEM analysis and the presence of water in the inter layer region (confirmed from IR studies) allowed the penetration of rubber molecules into the inter layer spacing. The reinforcing effect of MLS2 was less than that expected. This might be due to the agglomeration of the particles as seen in the TEM images.
Dry rubber composites showed superior properties than the latex based composites. Tendency of the silicates to agglomerate might have contributed to the decline in properties of the latex based composites. Stephen, R. et al. have suggested that absence of mastication step in the preparation of latex composites lead to the decline in properties. Mastication helped in the formation of free radical sites in rubber molecules and these labile free radicals could interact with the surface of filler particles resulting in a bonded structure [21], enhancing the properties of the dry rubber composites.
Table 8.2 gives the percentage increase in the mechanical properties of NBR produced by the incorporation of LS1 and LS2. The polar nature of NBR contributed to strong rubber-filler interaction leading to stress transfer from rubber matrix to filler particles. On the basis of the increase in the tensile strength and elongation at break it could be inferred that an organic/inorganic net work structure existed throughout the composite, eventhough the layered silicates were not covalently bonded to the polymer matrix. The increase in tear strength of NBR by the addition of layered silicate LS1 might be due to the special layer structure of the silicate in the composite leading to interfacial sliding between the silicate layers and NBR matrix.

Table 8.2. Percentage increase in the mechanical properties of NBR produced by the incorporation of the layered silicate LS1 and LS2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Layered silicate(LS1)</th>
<th>Layered silicate(LS2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>95</td>
<td>44</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>74</td>
<td>16</td>
</tr>
<tr>
<td>Modulus</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td>Tear strength</td>
<td>7</td>
<td>50</td>
</tr>
</tbody>
</table>

8.8 Conclusions

Incorporation of LS2 enhanced the tensile strength of NBR by 100% and SBR by 119%. Elongation at break increased by 74% with NBR and 91% with SBR respectively. Thus the silicate LS2 was found to be good reinforcing filler in NBR and SBR. Organomodified silicate did not give an expected result, might be due to the agglomeration of the silicate formed. The incorporation of all these fillers declined the properties of latex composites especially XNBR latex. Lack of proper dispersion of filler and the tendency for the silicates to agglomerate in latex medium might have contributed to the decline in properties of the latex composites.
Chapter 8

References


Preparation of layered silicates, its characterization and use in XNBR/SBR lattices and NBR/SBR dry rubber


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