5.1 Introduction

Styrene butadiene rubber (SBR) is one of the most versatile synthetic rubber compounds, produced by the copolymerisation of styrene and butadiene. The important limitations of SBR are poor strength, low resilience, low tear strength and poor tack. For amorphous polymers like SBR which does not undergo strain induced crystallisation, the use of fillers can improve the processability and mechanical properties and thus reduce the cost of rubber articles [1].

Among the vast nanofillers available for fabricating polymer nanocomposites, clay has been focussed and studied the most due to its easy availability, low cost, special stratified structure, high surface area, high aspect ratio etc.

SBR based nanoclay composites have been reported by several authors [2-6]. Wonho Kim et al. [4] used octadecyl amine modified MMT to prepare SBR composites by latex coagulating and melt mixing methods.
According to Kim, though compounding by melt mixing is an environmentally friendly method, it is very difficult to intercalate rubbery materials into the clay galleries. While in the latex method swellable clays like MMT are easily exfoliated by dispersing in deionized water and the high molecular weight polymer chain need not penetrate the galleries of the silicate. Other benefits include easy use of rubber in the form of latex and maximum dispersing effect of MMT in solution and the use of water as solvent.

Composites based on carbon nanotube have attracted great interest due to their unique mechanical, surface, electrical and multi functional properties. The improvement in properties is observed due to the nano-scale microstructure and extremely large interfacial area of the nanotubes [7]. The most common methods employed to prepare nanotube/polymer composites are solution blending, melt blending and insitu polymerisation. Of these, solution blending is most amenable to small sample sizes and is an effective method [8].

Studies of elastomeric composites with MWCNT include MWCNT/NBR/SBR composites prepared by melt mixing on a two roll mill [9], MWCNT/NR composites prepared by solvent mixing method using toluene as the solvent [10] and MWCNT/methyl vinyl silicone rubber composites prepared by solution method [11].

The major challenges encountered in developing high performance polymer/carbon nanotube composites are, homogeneous dispersion of carbon nanotubes and strong interfacial interactions to ensure efficient load transfer from the polymeric matrix to the carbon nanotubes. Carbon nanotubes usually exist as bundles with vander Waals forces holding the
tubes together [12]. The yield strength of the composite is related to the morphology, domain size, and size homogeneity of the nanotube in the matrix [13].

A review on recent advances in graphene based polymer nanocomposites discusses the effectiveness of graphene as nanofiller in various polymeric matrices like epoxy, polystyrene, polyaniline, polyurethane, poly(vinylidenefluoride), polycarbonate, PET etc. [14]. Reports on elastomer based graphene composites are limited. Zhan et al. [15] prepared NR/graphene composites by a latex stage mixing method, and in situ reduction process of the graphene oxide. Graphite powder with different forms and sizes were mixed in NBR using a twin roller by Jian Yang [16]. Wang et al. [17] prepared NBR composites with expanded graphite by latex compounding and mechanical mixing. Amit Das et al. [18] mixed solution of styrene butadiene rubber with graphene nanoplatelets, expanded graphite and carbon nanotubes using an internal mixer. Kim et al. [19] prepared SBR based graphene nanocomposites by solution mixing method.

Pristine graphene as a bulk material has a tendency to agglomerate in a polymer matrix, so they are unsuitable as such for intercalation by polymer materials. But they can be easily dispersed in suitable solvents like water, acetone, chloroform, tetrahydrofuran (THF), dimethylformamide (DMF) etc. owing to their weak forces that stack the layers together.

Graphite is composed of stacks of parallel two dimensional graphene sheets with sp² hybridized carbon atoms tightly bonded in hexagonal rings. The adjacent graphene sheets are held together by weak van der Waals forces [20]. Graphene nanoplatelet is not an individual graphene sheet but comprises...
of multiple graphene sheets that are stacked together [21, 18]. Thus, the thickness of the platelets is significantly larger than individual graphene sheet.

In this chapter the effect of addition of different nanofillers like nanokaolin, vinylsilane grafted nanokaolin, multiwalled carbon nanotube and graphene nanoplatelets in SBR latex are discussed. SBR based nanocomposites were prepared by a latex blending technique. SBR latex was mixed with aqueous dispersion of nanofillers and other compounding ingredients and cast in glass trays. The casting was allowed to dry in air and then vulcanized in air circulated oven.

5.2 Experimental
5.2.1 Materials

SBR latex - Encord 204, supplied by Jubilant Organosys Ltd., Gujarat. Specification of SBR latex is given in Table 2.2. Nanokaolin (Nanocaliber100) and Vinylsilane grafted nanokaolin (Nanocaliber 100V), were supplied by English Indian Clays Ltd., Veli, Thiruvananthapuram. Specification is given in Table 2.3. Multiwalled carbon nanotube (MWCNT) - Baytube R 150P was obtained from Baeyer Materials Science AG (Leverkusen Germany). Specification is given in Table 2.4. Graphene nanoplatelets were purchased from Quantum materials Ltd., Bangalore.

Nanokaolin is designated as ‘C’ and SBR composites containing 1, 5, 10 phr ‘C’ are referred as SBR-1C, SBR-5C, SBR-10C etc. Vinylsilane grafted nanokaolin is designated as ‘V’ and SBR containing 1, 5, 10 phr V are represented as SBR-1V, SBR-5V, SBR-10V etc and graphene nanoplatelets are referred as graphene.
5.2.2 Preparation of SBR based nanocomposites

Formulations used for making SBR latex compounds are given in Table 3.4. Preparation of SBR latex/clay nanocomposites and SBR/MWCNT/graphene nanocomposites are given in Section 3.11.1. and Section 3.11.3 respectively.

5.2.3 Methods

Detailed description of the methods used for the study of the mechanical properties (Section 2.4.5), swelling studies (Section 2.4.6), TGA (Section 2.4.8), DSC (Section 2.4.9), XRD (Section 2.4.10), FTIR (Section 2.4.11), SEM (Section 2.4.13) and AFM (Section 2.4.16) are included in Chapter 2.

5.3 Results and Discussion

5.3A Nanokaolin in SBR Latex

Aqueous dispersion of nanokaolin was sonicated for 30min and added to SBR latex in concentrations ranging from 0-20phr. Latex stage blending technique adopted for the preparation of XNBR-C nanocomposites resulted in good interaction of hydrophilic clay with SBR latex. There was an appreciable increase in tensile strength, elongation at break, modulus and tear strength of the nanocomposites. Thermal stability and $T_g$ increased by increasing the concentration of nanokaolin. SBR/nanokaolin composites were characterized by XRD, FTIR, SEM and AFM analysis.

5.3A.1 Mechanical properties

Tensile properties of polymer–clay composite vulcanizates depend on several factors, including the extent of clay dispersion, the degree of
interfacial adhesion between the clay platelets and the polymer matrix as well as the extent of crosslink density [22].

For SBR-nanokaolin composites, tensile strength, elongation at break and modulus at 300% elongation increased with increase in the concentration of nanokaolin reached a maximum value and then decreased. Fig. 5.1 shows the variation of mechanical properties with clay loading.

Strong interaction of hydrophilic clay with SBR latex resulted in the reinforcement in properties. When the concentration of clay was above a critical level, aggregates were formed resulting in poor dispersion of clay. This led to degradation in mechanical properties of the nanocomposite at higher concentration [23]. Tear strength continuously increased with the concentration of clay. The special layer structure of the clay in the composites led to interfacial sliding between the clay layers and SBR matrix. This could decrease the energy of expansion of the crack, resulting in an increase in tear strength with concentration [5, 6]. The maximum % increase in the tensile properties along with their composition is given in Table 5.1.

Table 5.1. Percentage increase in mechanical properties of SBR-C nanocomposites

<table>
<thead>
<tr>
<th>Properties</th>
<th>Maximum % increase</th>
<th>Composition of nanokaolin (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>87</td>
<td>15</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>47</td>
<td>15</td>
</tr>
<tr>
<td>Modulus</td>
<td>55</td>
<td>15</td>
</tr>
<tr>
<td>Tear strength</td>
<td>119</td>
<td>20</td>
</tr>
</tbody>
</table>
5.3A.2 Swelling studies

The variation in solvent uptake with increase in concentration of naokaolin was studied using toluene as the solvent. The diffusion curves were plotted as $Q_t$, mole % uptake per 100g of the solvent against time. From Fig. 5.2 it is found that gum has the maximum uptake at equilibrium. Swelling rate of the nanocomposites decreased with increase in concentration of clay. The clay platelets were distributed in the polymer matrix in multiple parallel layers. These impenetrable clay layers forced the solvent molecules to flow through the polymer in a “torturous path”, forming complex barriers to the solvent molecules [24].
5.3A.3 Thermogravimetric analysis (TGA)

Fig. 5.3 shows the TGA curve and Table 5.2 gives the thermal analysis data of unfilled and filled SBR. The temperature of onset of degradation of SBR shifted from 320°C to 337°C by the addition of 15phr nanokaolin. Maximum degradation temperature, Tmax and the temperature at 10% (T10), 25% (T25) and 50% (T50) weight loss were shifted to higher temperature in SBR-15C nanocomposite. This showed the thermal stability of the composite increased by the addition of nanoclay. It is generally observed that the inclusion of inorganic components into organic materials improves the thermal stability of the polymer [25]. The observed increase in the thermal stability of SBR-15C nanocomposite was due to the high thermal stability of nanoclay and good interaction between the clay layers and polymer matrix through intercalation/exfoliation. The intercalated polymer chains were covered by clay layers which prevents the direct exposure of the chains to thermal influence.

Table 5.2 Thermal analysis results of SBR and SBR-15C nanocomposite

<table>
<thead>
<tr>
<th>Name</th>
<th>Onset temp. (°C)</th>
<th>Peak max. T_{max} (°C)</th>
<th>T_{10} (°C)</th>
<th>T_{25} (°C)</th>
<th>T_{50} (°C)</th>
<th>Residue %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>320</td>
<td>441</td>
<td>365</td>
<td>398</td>
<td>426</td>
<td>3.08</td>
</tr>
<tr>
<td>SBR-15C</td>
<td>337</td>
<td>444</td>
<td>372</td>
<td>402</td>
<td>432</td>
<td>13.92</td>
</tr>
</tbody>
</table>

Fig. 5.3. TGA curve of SBR and SBR-15C nanocomposite
5.3A.4 Differential scanning calorimetry (DSC)

Glass transition temperature of SBR and SBR-15C nanocomposite is given in Table 5.3. DSC curve of SBR latex showed Tg at -16°C whereas the composite showed a small increase in Tg. The increase in Tg might be due to the effect of dispersed clay on the free volume of the polymer and the confinement of intercalated/exfoliated polymer chains within the clay galleries which resist the segmental motion of the polymer chains [26]

Table 5.3. Tg values of SBR and SBR-15C nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>-16</td>
</tr>
<tr>
<td>SBR-15C</td>
<td>-14</td>
</tr>
</tbody>
</table>

5.3A.5 X-ray diffraction analysis (XRD)

XRD spectra of nanokaolin (‘C’) and SBR-15C nanocomposite are given in Fig.5.4. The presence of a broad peak in the composite is an indication of exfoliation. Due to the greater compatibility of the hydrophilic nanokaolin with SBR latex, the polymer chain is more effective in causing exfoliation of clay. A very small peak with a larger spacing (d=9.22Å) was also seen in the nanocomposite, which confirmed intercalation in a very small number of clay particles.
5.3A.6 Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum of SBR-15C and SBR is given in Fig. 5.5 and Fig. 5.6 respectively. The intensities of the peaks at 2916 and 2844 cm\(^{-1}\) attributed to the CH stretching of aromatic rings in SBR and the peaks in the range 1400-1600 cm\(^{-1}\) and 699 cm\(^{-1}\) referring to the styrene units, [27] had become sharper in the nanocomposite. The peak corresponding to the trans 1, 4 butadiene of the styrene unit at 968 cm\(^{-1}\) remained with almost the same intensity. Peaks at 1100, 1028 and 913 cm\(^{-1}\) in the composite correspond to the Si-O-Si, Al-O-Si units in nanokaolin. Intensity of characteristic OH stretching vibration of nanokaolin was reduced in the composite (FTIR spectrum of nanokaolin is given in Fig. 3.2). Reduction in the intensity of OH band in nanokaolin, and strengthening of bands due to styrene units showed the interaction of OH group of nanokaolin with the bulky styrene units of SBR.
5.3A.7 Scanning electron microscopy (SEM)

Fig. 5.7 (A) and (B) show the SEM images of SBR-15C nanocomposite at different magnification. From the SEM images it is seen that the clay platelets are well embedded in the matrix. At a still higher magnification a homogeneous dispersion having a continuous phase was visible (Fig 5.7(B)). This showed good compatibility and adhesion of clay with SBR latex.
5.3A.8 Atomic force microscopy (AFM)

Fig. 5.8 displays the AFM image of SBR-15C nanocomposite. A smooth surface with clay particles embedded in it and some clay aggregates locally confined in some areas are visible in the image.

![AFM image of SBR-15C nanocomposite](image)

Fig. 5.8. AFM image of SBR-15C nanocomposite.

5.3A.9 Conclusions

SBR/nanokaolin composites prepared by the latex stage blending showed good improvement in mechanical properties owing to the improved
dispersion of clay platelets. Intercalation/exfoliation of clay layers took place during latex stage blending as observed by XRD analysis. The composite showed improved thermal stability.

5.3B Vinylsilane Grafted Nanokaolin in SBR Latex

Vinylsilane modified nanokaolin (V) was incorporated in SBR latex in concentrations varying from 0-25 phr. Vinylsilanes usually used for the treatment of clay are vinyl triethoxy silane and vinyl trimethoxy silane. The alkoxy groups are hydrolytic groups which are hydrolyzed to silanol groups in presence of water or moisture [28-30]. These silanol groups can form covalent bonds with some of the OH groups on the edge surface of clay by a condensation mechanism, or they can form hydrogen bonds with the OH groups in clay, while the vinyl groups can interact with the polymer chains. This is schematically represented in Fig.1.6. This interaction will give a reinforcing effect for the modified clay in SBR latex. SBR latex/vinylsilane grafted nanokaolin composites have not been reported so far. Mechanical/thermal properties and characterization of SBR latex/vinyl silane grafted nanokaolin composites are discussed here.

5.3B.1 Mechanical Properties

Fig.5.9 (A) and (B) shows the variation of tensile strength/elongation at break and modulus/tear strength of the nanocomposite with clay (‘V’) loading (0-25 phr). Table5.4 gives the percentage increase in the mechanical properties of the nanocomposite at various filler loading. The addition of clay at lower loading did not produce any significant increase in tensile strength due to the lack of proper dispersion of the filler. Tensile strength of SBR-V nanocomposite was found to be smaller
than that of SBR-C nanocomposite. This is because organic modification of nanokaolin had made it organophilic and hydrophobic. This decreased the compatibility of clay with SBR latex, causing a reduction in the tensile strength.

The decrease in elongation at break by the inclusion of rigid filler in a soft matrix is a common observation [31, 32]. Incorporation of fillers with poor adhesion to the polymer matrix weakens interfacial regions between filler surfaces and rubber matrix causing a reduction in the elongation at break.

An increase in modulus was expected due to the decrease in elongation at break. Although compatibility between modified clay and rubber latex was low, there was interaction between the non polar SBR and the vinyl group of clay. This led to an increase in modulus value.

Tear strength of SBR-V nanocomposite increased with the modified clay loading. This was attributed to the layer structure of nanoclay [33].

Fig. 5.9. Variation of (A) Tensile strength/Elongation at break and (B) Modulus/Tear strength of the nanocomposite with clay ‘V’ loading
Table 5.4. Percentage increase in mechanical properties of SBR-V nanocomposite

<table>
<thead>
<tr>
<th>Properties</th>
<th>%increase</th>
<th>Composition of V (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength(MPa)</td>
<td>43</td>
<td>20</td>
</tr>
<tr>
<td>Modulus(MPa)</td>
<td>98</td>
<td>20</td>
</tr>
<tr>
<td>Tear strength (%)</td>
<td>119</td>
<td>20</td>
</tr>
</tbody>
</table>

5.3B.2 Swelling studies

Fig. 5.10 gives the variation of $Q_t$, mole % with Time$^{1/2}$. When compared to SBR-C nanocomposites, SBR-V nanocomposites showed greater swelling rate. This is because the compatibility of the organophilic clay in SBR latex was less than that of unmodified clay. So there was more filler–filler interaction and more chances to form filler aggregates. As a result the clay platelets might not be fully available in the matrix to enhance the tortuosity of the path.

![Fig. 5.10. Sorption curves of SBR-V nanocomposites](image)

5.3B.3 Thermogravimetric analysis (TGA)

TGA curves for SBR and its composites containing 10 phr and 20 phr vinylsilane grafted nanokaolin are given in Fig. 5.11 and their thermal analysis
data are given in Table 5.5. Onset temperature increased with increase in clay loading. \(T_{10}, T_{25}\) and \(T_{50}\) showed gradual increase with the addition of clay, while \(T_{\text{max}}\) remained a constant. The thermal stability obtained by the addition of modified clay in SBR was less than that obtained by the addition of unmodified clay. This might be due to the reduction in the polymer filler interaction in SBR/modified clay nanocomposite. Percentage of residue remaining at 700\(^\circ\)C increased with the increase in clay loading. At higher clay loading the interaction between clay and SBR increased and the matrix became stiffer and thus the diffusion of heat and gases through the bulk became more difficult. This prevented the complete degradation of the nanocomposite.

Table 5.5. Thermal analysis results of SBR and SBR-15V nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp. ((^\circ)C)</th>
<th>Peak max. ((^\circ)C)</th>
<th>Residue (%)</th>
<th>(T_{10}) ((^\circ)C)</th>
<th>(T_{25}) ((^\circ)C)</th>
<th>(T_{50}) ((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>320</td>
<td>441</td>
<td>3.08</td>
<td>365</td>
<td>398</td>
<td>426</td>
</tr>
<tr>
<td>SBR -10V</td>
<td>328</td>
<td>438</td>
<td>9.32</td>
<td>366</td>
<td>400</td>
<td>430</td>
</tr>
<tr>
<td>SBR- 20V</td>
<td>330</td>
<td>440</td>
<td>12.67</td>
<td>371</td>
<td>402</td>
<td>433</td>
</tr>
</tbody>
</table>

Fig. 5.11. TGA curves of SBR-V nanocomposite
5.3B.4 Differential scanning calorimetry (DSC)

DSC analysis data of SBR and SBR-V nanocomposite is given in Table 5.6. SBR-V nanocomposite gave a very small increase in $T_g$ with the incorporation of modified clay, showing that the SBR chain mobility was restricted in the nanocomposite.

**Table 5.6. Glass transition temperature of SBR and SBR-20V nanocomposite**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>-16</td>
</tr>
<tr>
<td>SBR-20V</td>
<td>-15</td>
</tr>
</tbody>
</table>

5.3B.5 X-ray diffraction analysis (XRD)

Insertion of polymer chains in the interlayer space of clay causes an increase in the interlayer volume and a shift in the diffraction peaks to lower angles. Diffraction peaks will be absent in case of exfoliation, when the clay layers are completely and uniformly dispersed in the polymer matrix [34].

Fig. 5.12 gives the XRD patterns of ‘V’ and SBR-20V nanocomposite. The nanocomposite showed only a slight shift in the 20 angle with a small increase in d spacing. The d spacing increased from 7.1 to 7.5 Å and from 3.56 to 3.58 Å in the nanocomposite. The peak at 20 value 20° was also very much reduced in the nanocomposite formed. The presence of bulky styrene ring in the polymer chain would have slightly restricted the intercalation of polymer chain into the interlayer space of clay. This showed the intercalation of SBR into the clay layers was insignificant. The reduced compatibility between the hydrophobic organo modified clay and the hydrophilic SBR latex prevented the exfoliation of clay.
Fig.5.12.  X-ray diffraction pattern of vinylsilane grafted nanokaolin (V) and SBR-20V nanocomposite

5.3B.6 Fourier transform infrared spectroscopy (FTIR)

IR spectrum of SBR-20V nanocomposite is given in Fig 5.13. The characteristic OH stretching bands of nanokaolin (Fig 3.6) in the range 3600-3690cm\(^{-1}\) were seen in the nanocomposite also. Peaks due to CH\(_2\) symmetric and asymmetric stretching (2916 and 2844cm\(^{-1}\)) in SBR (Fig.5.6) had become sharper in the nanocomposite due to the interaction of vinyl group of clay with the CH\(_2\) group of rubber back bone. A medium peak at 1447cm\(^{-1}\) represented the merging of CH\(_2\) groups of rubber with the vinyl groups of clay. The peak at 1095cm\(^{-1}\) showed the C-O stretch of alcoholic groups in clay. Appearance of a very strong band at 1023cm\(^{-1}\) was due to Si-O-Si (siloxane network) stretching vibration of clay [35]. The peak due to butadiene double bond in SBR at 963cm\(^{-1}\) was very much reduced in the nanocomposite. This might be due to the interaction of butadiene double bond with the double bonds of vinyl group in the modified clay.
5.3B.7 Scanning electron microscopy (SEM)

Fig. 5.14 shows the SEM photograph of SBR-V nanocomposite. The particles seem to project out from the matrix showing less compatibility of modified clay particles with the matrix.

5.3B.8 Conclusions

Vinylsilane grafted nanokaolin enhanced the tensile strength, modulus and tear strength of SBR. Enhancement in properties were less in SBR-V compared to SBR-C nanocomposite. XRD data showed that the intercalation of polymer chain with the bulky styrene group led to an
insignificant increase in the interlayer spacing. SEM images also proved the low compatibility of modified clay with SBR latex. Thermal studies showed an improvement in the thermal stability of the nanocomposite and a slight increase in the glass transition temperature. FTIR analysis showed the interaction of vinyl groups in clay with the butadiene double bonds of the polymer chains.

**5.3C MWCNT in SBR Latex**

When mixed with rubber, carbon nanotubes usually give a poor dispersion, due to agglomeration of nanotubes by van der Waals forces. Any agglomeration results in the reduction of properties of the composite as it prevents efficient stress transfer to individual nanotubes. Here, an efficient dispersion of MWCNT was made by sonication in presence of a cationic surfactant SDBS. Introduction of functional groups on the nanotube surface during purification process improved the affinity to water and was beneficial for the preparation of MWCNT dispersion in SDBS. Moreover the functional groups loaded on the nanotube surface assisted in the interfacial bonding between carbon nanotube and SBR latex causing enhancement in the mechanical properties of the composite. MWCNT was added only in very small concentration to SBR latex. The nanocomposites prepared were characterized and their properties studied in detail.

**5.3C.1 Mechanical Properties**

Fig.5.15 (A) and (B) shows the variation in mechanical properties of SBR by the addition of MWCNT and Table5.7 gives the percentage increase in the mechanical properties. The addition of MWCNT brought about remarkable increase in tensile strength, elongation at break, modulus and tear
strength. This confirmed that MWCNT carried stress throughout the rubber matrix and played an effective role in the reinforcement of the nanocomposite.

MWCNT was added to SBR latex only in very small concentration ranging from 0-1.5 phr. Even with the very small concentration, tensile strength increased by 65%, elongation at break by 41%, modulus by 95% and tear strength by 68%. Well dispersed nanotube and good interface between the nanotube and SBR matrix led to the increase in tensile strength of the nanocomposite [36]. High Young’s modulus and strength of the well dispersed nanotubes led to the increase in tear strength and modulus of the nanocomposite [7].

![Graph showing variation of properties](image)

Fig.5.15. Variation of (A) Tensile strength and Elongation at break (B) Modulus and Tear strength of SBR-MWCNT nanocomposite

Table 5.7. Percentage increase in mechanical properties of SBR-MWCNT nanocomposites

<table>
<thead>
<tr>
<th>Properties</th>
<th>% increase</th>
<th>Composition of MWCNT (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>65</td>
<td>1.5</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>41</td>
<td>1</td>
</tr>
<tr>
<td>Modulus</td>
<td>95</td>
<td>1.5</td>
</tr>
<tr>
<td>Tear strength</td>
<td>68</td>
<td>1</td>
</tr>
</tbody>
</table>
5.3C.2 Swelling studies

Fig 5.16 gives the variation of Qt (%) with T^{1/2}. The swelling rate of the nanocomposite containing 0.5 phr MWCNT was found to be greater than SBR without filler. This might be because the surfactant SDBS used for the preparation of MWCNT dispersion might have created a weak interface at the low concentration of nanotube and must have assisted in the penetration of the solvent. But with the increase in concentration of MWCNT, the effect of the interphase diminished and the distribution of MWCNT in the matrix prevented the penetration of the solvent leading to a decrease in the swelling rate.

![Swelling study graph](image)

Fig. 5.16. Sorption curves of SBR-MWCNT nanocomposites

5.3C.3 Thermogravimetric analysis (TGA)

TGA trace of the nanocomposite containing 0.15phr MWCNT and SBR are shown in Fig.5.17. From Table 5.8 it is seen that the onset degradation temperature, Tmax and temperature at 5% and 50% weight loss are higher for the nanocomposite, showing that it is thermally more stable. As suggested by M. Moniruzzaman in a review on ‘Polymer nanocomposites containing carbon nanotubes’ the dispersed nanotubes might hinder the flux of degradation product
and thereby delay the onset of degradation. Polymers near the nanotube degrade more slowly which would shift the Tmax to higher temperature and the effect of higher thermal conductivity in the nanotube/polymer composites facilitates heat dissipation within the composite. All these factors might have contributed to the thermal stability of the SBR-MWCNT nanocomposite [8].

Table 5.8. Thermal analysis results of SBR and SBR-0.15MWCNT

<table>
<thead>
<tr>
<th>Samples</th>
<th>On set temp. (°C)</th>
<th>Tmax (°C)</th>
<th>Temp. At 5%wt.loss (°C)</th>
<th>Temp. at 50%wt.loss (°C)</th>
<th>Residue %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>320</td>
<td>441</td>
<td>313</td>
<td>426</td>
<td>3.08</td>
</tr>
<tr>
<td>SBR-0.15MWCNT</td>
<td>331</td>
<td>450</td>
<td>325</td>
<td>430</td>
<td>4.65</td>
</tr>
</tbody>
</table>

Fig. 5.17. TGA curves of SBR and SBR-0.15MWCNT nanocomposite

5.3C.4 Differential scanning calorimetry (DSC)

Table 5.9 gives the Tg of SBR and SBR containing 0.15phr MWCNT. Tg of the nanocomposite decreased with the addition of MWCNT. The decrease in Tg showed the labile nature of polymer chains and the weak interaction among SBR molecular chains in the nanocomposite. Lipatov has suggested that the chain mobility depends on the polymer cohesive forces. In
non polar elastomers, the cohesive forces are low and therefore only minor changes in $T_g$ were expected for carbon nanotube SBR composites [9]

Table 5.9. $T_g$ values of SBR and SBR-0.15MWCNT nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>-16</td>
</tr>
<tr>
<td>SBR-0.15 MWCNT</td>
<td>-17</td>
</tr>
</tbody>
</table>

5.3C.5 Fourier transform infrared spectroscopy (FTIR)

IR spectrum of the SBR-MWCNT nanocomposite (Fig.5.18) showed strong peaks at 2916 cm$^{-1}$ and 2849 cm$^{-1}$. This might be due to a synergetic effect of CH stretch on SBR by the addition of MWCNT. The medium peak at 1546 cm$^{-1}$ is the stretching mode of C=C of MWCNT. The sharp, strong peak at 699 cm$^{-1}$ showed the interaction of styrene units of SBR with MWCNT. (FTIR of SBR is given in Fig 5.6 and MWCNT is given in Fig.3.11)

Fig.5.18. FTIR spectrum of SBR-MWCNT nanocomposite
5.3C.6 Scanning electron microscopy (SEM)

The tear fractured surface of the nanocomposite is shown in Fig.5.19. The surface seems to be rough with a number of ridge lines indicating the direction of crack propagation. These ridgelines of reinforcement indicate good compatibility of MWCNT and polymer matrix.

![SEM images of SBR-MWCNT nanocomposite](image)

Fig.5.19. SEM images of SBR-MWCNT nanocomposite

5.3C.7 Conclusions

There was remarkable improvement in mechanical properties of SBR with the addition of nanotube at a loading as low as 1.5phr. Tensile strength showed 65% increase while modulus and tear strength gave 95% and 68% increase respectively. Thermal stability of the nanocomposite increased by the addition of MWCNT.

5.3D Graphene Nanoplatelets in SBR Latex

Naturally occurring graphite being a source material for graphene nanoplatelets, is gaining prominence as an ideal reinforcing material to improve polymer properties. 2D confinement of graphene platelets to polymer matrix and its high surface area makes it a superior nanofiller in the field of material science. Graphene nanoplatelet is not an individual
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graphene sheet but comprises multiple graphene sheets that are stacked together [18, 21]. Thus, the thickness of the platelets is significantly larger than an individual graphene sheet.

Effect of graphene on the mechanical and thermal properties of SBR latex is discussed. The composites are characterized by XRD, FTIR and SEM analysis.

5.3D.1 Mechanical properties

Fig. 5.20 gives the variation of tensile strength/elongation at break and modulus/tear strength of SBR/graphene nanocomposite. Table 5.10 gives the % increase in the mechanical properties of the nanocomposites. Tensile strength increased by 66% and modulus by 110% by the addition of 1phr graphene. Improvement in the mechanical properties of graphene containing nanocomposite depends on the distribution of graphene layers in the polymer matrix, interfacial bonding between the graphene layers and polymeric matrix [14] and the alignment of graphene in the matrix [37].

Graphene dispersion prepared in vulcastab might be considered as comprising of graphene platelets surrounded by an interphase [37]. From the SEM images it appears that graphene platelets are enveloped by a fine glazing, fur like covering (Fig.5.24)

Formation of an interphase around the platelets might enhance stress transfer [38]. So even in the absence of a covalent bonding between the filler and the matrix the presence of the interphase assisted in the reinforcement in properties. The SEM images also showed a uniform distribution of graphene. Increase in elongation at break might be attributed to the sliding effect of graphene platelets, which could be taken as a plasticization effect
[39]. All these contributed to the enhancement in the mechanical properties of the composite.

![Variation of (A) Tensile strength and Elongation at break (B) Modulus and Tear strength of SBR-graphene nanocomposite](image_url)

**Fig.5.20.** Variation of (A) Tensile strength and Elongation at break (B) Modulus and Tear strength of SBR-graphene nanocomposite

**Table 5.10.** Percentage increase in mechanical properties of SBR-graphene nanocomposites

<table>
<thead>
<tr>
<th>Properties</th>
<th>% increase</th>
<th>Composition of graphene (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>66</td>
<td>1</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>45</td>
<td>0.5</td>
</tr>
<tr>
<td>Modulus</td>
<td>110</td>
<td>1</td>
</tr>
<tr>
<td>Tear strength</td>
<td>66</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### 5.3D.2 Swelling studies

Fig.5.21 shows the sorption curves of SBR graphene nanocomposites. Here the swelling rate of nanocomposites was found to be higher than that of SBR without filler. Similar abnormal behaviour was reported in blends of NR/XSBR [40]. The presence of vulcastab envelopping the graphene platelets might have created a weak interphase which assisted in the penetration of the solvent resulting in an increase in the swelling rate.
5.3D.3 Thermogravimetric analysis (TGA)

$T_{\text{max}}$, $T_{10}$, $T_{25}$ and $T_{50}$ values decreased showing that the graphene platelets could not transfer heat properly. The small decrease of thermal resistance is an evidence for the heterogeneity and lack of filler protective action [41] in the nanocomposite.

Table 5.11. Thermal analysis results of SBR and SBR-0.05graphene

<table>
<thead>
<tr>
<th>Samples</th>
<th>On set temp. ($^\circ$C)</th>
<th>$T_{\text{max}}$</th>
<th>Temp. at wt.loss ($^\circ$C)</th>
<th>Residue%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_{10}$</td>
<td>$T_{25}$</td>
</tr>
<tr>
<td>SBR</td>
<td>320</td>
<td>441</td>
<td>365</td>
<td>398</td>
</tr>
<tr>
<td>SBR-0.05Graphene</td>
<td>322</td>
<td>436</td>
<td>355</td>
<td>391</td>
</tr>
</tbody>
</table>

5.3D.4 Differential scanning calorimetry (DSC)

Two competing effects on the chain mobility of the polymer matrix, at the interface of a nanofiller/polymer composite are (1) enhancement in
mobility caused by a larger free volume and (2) restriction in mobility caused by physical or chemical interaction with the filler. Free volume reduces $T_g$ while interaction with the filler produces an opposite effect [42].

From Table 5.12 it is seen that with the addition of graphene, $T_g$ of the nanocomposite first increased and then decreased. At low concentration there might be greater interaction between polymer chain and filler particles which restricted the mobility of the polymer chains leading to an increase in $T_g$. But when concentration of graphene increased, aggregation might have taken place leading to an increase in the free volume available in the composite. This led to the increase in the mobility of polymer chain and consequent decrease in $T_g$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>-16</td>
</tr>
<tr>
<td>SBR-0.3 Graphene</td>
<td>-14</td>
</tr>
<tr>
<td>SBR-0.5 Graphene</td>
<td>-16</td>
</tr>
<tr>
<td>SBR-1.0 Graphene</td>
<td>-19</td>
</tr>
</tbody>
</table>

5.3D.5 X-ray diffraction analysis (XRD)

Fig 5.22 gives the XRD diffraction pattern of graphene and SBR-graphene nanocomposite. Absence of peak in the nanocomposite is an indication of the complete exfoliation of graphene platelets.
5.3D.6 Fourier transform infrared spectroscopy (FTIR)

Fig. 5.23 shows the IR spectrum of SBR/graphene nanocomposite. Peaks at 2918 cm$^{-1}$ and 2844 cm$^{-1}$ represented the C-H stretch of aromatic rings, peak at 1590 cm$^{-1}$ showed the presence of C=C and the peaks at 962 and 695 cm$^{-1}$ gave the styrene units present in the nanocomposite.

Greater intensity of these peaks in the nanocomposite showed the interaction of pi electrons of graphene with the unsaturated sites in SBR.
(FTIR of SBR and graphene are shown in Fig.3.14 and Fig.5.6 respectively). The appearance of a new peak at 1105 cm\(^{-1}\) might be assigned to the C-O-C stretching ( dialkyl) of ether group from the surfactant vulkastab (polyethyleneoxide condensate).

5.3D.7 Scanning electron microscopy (SEM)

Fig.5.24 gives the SEM photographs of SBR-graphene nanocomposite. Graphene nanoplatelets were seen to be uniformly dispersed in the matrix. A shining glaze and a very fine feathery sheath was seen surrounding the graphene platelets. This might be the envelope created by the non ionic surfactant vulcastab around the graphene particles.

![SEM images of SBR-graphene nanocomposite](image)

5.3D.8 Conclusions

An aqueous dispersion of graphene was prepared using a novel surfacant vulcastab. The composite showed remarkable improvement in mechanical properties. Proper dispersion of graphene platelets in SBR might have enhanced stress transfer leading to reinforcement in properties. Increase in swelling rate by the penetration of the solvent might be attributed to the presence of a weak interface caused by the surfactant. FTIR spectrum showed the interaction of graphene platelets with the unsaturated sites in SBR matrix.
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References


[31] Ismail, H. Jaffri, R.M. Polymer Testing. 1999, 18, 381.


