6.1 Introduction

In unvulcanized raw rubber the polymer chains are long and flexible with an entangled and kinked structure. An uncured rubber cannot be used to make articles with a good degree of elasticity. Transformation of uncured rubber to useful rubber with unique physical and chemical properties is achieved by the process of vulcanization. On vulcanization physical and chemical cross links are formed between the polymer chains giving a three dimensional network structure. The inclusion of rigid entities increases stiffness and resistance to fracture due to interaction between the elastomer and filler surface. The properties and performance of the elastomeric nanocomposites depend on the structure of the polymer matrix, the cross linking chemistry of rubber, nature of nanofillers, the physical and chemical interaction of the fillers with the rubber matrix, the degree of filler dispersion in the rubber matrix and the methods by which they are prepared [1]. NBR because of its good processability, resistance to oils, fuel and chemicals, as well as excellent mechanical properties after vulcanization, is a good candidate for elastomer based nanocomposites.
Significant improvement in mechanical and barrier properties are obtained by the inclusion of nanosized silicates in elastomeric matrices. Efficiency of the silicates in modifying the properties of rubber depends on the degree of their dispersion and the extent of exfoliation in rubber. One advantage of rubber silicate nanocomposite is that the high shear stress generated locally during compounding of the very high molecular weight rubber material is beneficial to the delamination of the layered silicate [2].

Recently carbon nanotubes (CNTs) have become increasingly attractive due to the possibilities of large scale production of these materials. Multiwalled carbon nanotubes are widely used in industrial applications, because their production is less complex and more cost effective due to the consumption in low loading to achieve comparable composite properties [3]. The intrinsic potential of carbon nanotubes as reinforcing filler in elastomeric materials is given by Liliane Bokobza in a review on “Multiwall carbon nanotube elastomeric composites”[4].

Since high purity graphene can be obtained from plentiful resource of natural graphite by relatively convenient approaches [5], this cost effective nanofiller even replaces carbon nanotubes in many key applications [6].

In this Chapter NBR based nanocomposites were prepared using different fillers like nanokaolin, vinylsilane grafted nanokaolin, MWCNT and graphene nanoplatelets. Mixing of nanoclay in two roll mill and MWCNT/graphene in brabender plasticorder helped to get a uniform dispersion of filler in NBR. The effect of these nanofillers on the cure behaviour, mechanical properties and thermal properties were studied in detail. The composites formed were characterized by XRD, FTIR and SEM analysis.
6.2 Experimental

6.2.1 Materials

NBR: Nitrile rubber is Kumho NBR (KNB 35L) supplied by Kumho Petrochemicals Co., Ltd. South Korea. It has acrylonitrile content (% by weight) 34 and Mooney viscosity ML (1+4) at 100°C=41

Nanokaolin is Nanocaliber100 and vinylsilane grafted nanokaolin is Nanocaliber 100V supplied by English Indian Clays Ltd. Veli, Thiruvananthapuram. Specification given in Table 2. Multiwalled carbon nanotube (MWCNT) - Baytube® 150P obtained from Bayer Materials Science AG (Leverkusen Germany). Specification given in Table 2.4. Graphene nanoplatelets were purchased from Quantum materials Ltd. Bangalore.

Nanokaolin is designated as ‘C’ and NBR compounds containing 1,5,10 phr nanokaolin is represented as NBR-1C, NBR-5C, NBR-10C etc. Vinylsilane grafted nanokaolin is represented as ‘V’ and the compounds containing 1,5, and 10phr vinylsilane grafted nanokaolin are designated as NBR-1V, NBR-5V, NBR-10V etc. Graphene nanoplatelets used are referred as graphene.

6.2.2 Preparation of NBR based nanocomposites

Formulation used for the preparation of NBR compounds is given in Table 3.5. Mixing and homogenization of the rubber compounds were done in a two roll mill and brabender plasticorder. Details for the preparation of NBR/clay nanocomposite, by mixing in a two roll mill is given in Section 3.11.4. Preparation of NBR/MWCNT/graphene nanocomposites by mixing in brabender plasticorder is given in Section 3.11.5. Cure characteristic of
the mixes were determined using Rubber Process Analyser (R PA 2000-Alpha Technologies) as per ASTM D 2084-1995B. Details of the cure study are given in Section 2.4.3. The test samples were further vulcanized in an electrically heated hydraulic press having 45 cm × 45 cm platen at 160°C at a pressure of 200Kg/cm² on the mould upto an optimum cure time. Moulded samples were conditioned for 24 hrs before testing.

6.2.3 Methods

Methods used for the study of mechanical properties are given in Section 2.4.5 and Swelling studies in Section 2.4.6. Thermal analysis were done in TA instruments (Section 2.4.8 & 2.4.9) and the characterization methods included XRD (Section 2.4.10), FTIR (Section 2.4.11) and SEM analysis (Section 2.4.13).

6.3 Results and Discussion

6.3A. Nanokaolin in NBR

Nanokaolin provides excellent reinforcement in rubber. Liu et al. [7] incorporated nanokaolin in SBR, NR, BR and EPDM and compared their reinforcing effect with that of precipitated silica (PS). Malicka-Soczka [8] studied the effect of both modified and unmodified kaolin in butadiene–styrene rubber (KER 1500). No further works on unmodified nanokaolin/elastomer composites were reported.

This part deals with the study of the reinforcing effect of nanokaolin (C) on the mechanical properties of NBR. Cure characteristics, swelling studies, strain sweep studies, thermal studies were also considered. The composites were characterized by XRD, FTIR and SEM analysis.
6.3A.1 Curing Studies

Fig. 6.1 shows the cure graphs of NBR-C nanocomposites containing different concentrations of nanokaolin (0, 1, 10 and 20 phr) at 160°C. As a general trend torque initially decreases, then increases and finally levels off. The initial decrease is due to the softening of the rubber matrix, the increase in torque value is due to the cross linking of rubber and the levelling off is an indication of completion of curing.

Vulcanization characteristics expressed in terms of minimum and maximum torque, optimum cure time (T90), scorch time (T10) and cure rate index (CRI) of NBR and nanokaolin filled NBR are given in Table 6.1. The increase in cure time, scorch time and decrease in CRI values were an indication of the cure retarding effect of nanokaolin. The adsorption of curatives on the surface OH groups of nanokaolin decreased the effective concentration of curatives leading to an increase in the optimum cure time. The increase in scorch time denoted the processing safety of the vulcanizate.

Maximum torque $M_H$ is a measure of shear modulus [9]. It gives the extent of cross linking reaction and a measure of filler polymer interaction. Increase in $M_H$ with filler loading showed improved interaction behaviour and good interfacial adhesion between matrix and filler.

Minimum torque is related to the viscosity of the compound. It measures the stiffness of the unvulcanized compound. The decrease in $M_l$ value suggested that the incorporation of filler did not impose any restriction to the molecular motion of the macromolecular polymer chain.
Fig. 6.1. Rheographic curves of NBR-C nanocomposites

Table 6.1. Cure properties of NBR-C nanocomposites

<table>
<thead>
<tr>
<th>Concentration of nanokaolin (phr)</th>
<th>Min. Torque $M_L$ (dNm)</th>
<th>Max. Torque $M_H$ (dNm)</th>
<th>Opt. cure time $T_{90}$ (min)</th>
<th>Scorch time $T_{10}$ (min)</th>
<th>Cure Rate Index $CRI$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.160</td>
<td>2.673</td>
<td>1.30</td>
<td>0.49</td>
<td>124</td>
</tr>
<tr>
<td>1</td>
<td>0.101</td>
<td>3.54</td>
<td>3.16</td>
<td>1.44</td>
<td>58.14</td>
</tr>
<tr>
<td>10</td>
<td>0.101</td>
<td>3.644</td>
<td>3.04</td>
<td>1.39</td>
<td>60.60</td>
</tr>
<tr>
<td>15</td>
<td>0.124</td>
<td>3.680</td>
<td>3.13</td>
<td>1.42</td>
<td>58.48</td>
</tr>
<tr>
<td>20</td>
<td>0.104</td>
<td>3.896</td>
<td>2.97</td>
<td>1.19</td>
<td>56.18</td>
</tr>
</tbody>
</table>

6.3A.2 Mechanical properties

Variation of tensile strength and elongation at break of NBR-C nanocomposites at different concentration of nanokaolin are shown in Fig. 6.2(A). The variations of modulus and tear strength of the composites are given in Fig. 6.2(B). A remarkable increase in the mechanical properties of nanocomposites was observed. Tensile strength, elongation at break, modulus at 300% elongation and tear strength increased by 56%, 30%, 17% and 49% respectively at 15 phr nanokaolin.
Interaction between clay platelets having large surface area and the polymer chains facilitated stress transfer, resulting in improved tensile properties [10]. Tensile strength and elongation at break were found to reach a maximum at 15 phr loading and after that properties declined with increase in concentration of the filler. The increase in tensile strength might be due to the increase in interfacial bonding of clay platelets and good interaction between the clay platelets and NBR. Increase in interfacial bonding arose by intercalation or possible exfoliation of clay layers, as evidenced by XRD analysis. The nanokaolin layers are linked through hydrogen bonding between hydroxyl groups on the octahedral sheet and oxide arrangement of tetrahedral sheet. Even though the intercalation reactivity of kaolin was low due to hydrogen bonding between the layers, the free OH groups on kaolin could interact with the CN groups of NBR. Decrease in tensile strength at higher loading might be due to agglomeration of clay tactoids, leading to stress concentration.

In contrast to other conventional fillers elongation at break of NBR-C nanocomposite was found to increase with clay concentration upto 15 phr. Better filler dispersion and strong rubber-filler interaction led to an increase in elongation at break. With the increase in rubber-filler interaction, decoiling of rubber chain might have taken place, leading to greater adsorption of energy by rubber molecules and slippage of clay particles. At higher loading the elongation at break decreased because of filler aggregation. Aggregation of filler weakens the number of available reinforcing links. The formation of non exfoliated aggregates at higher clay content made these composites much more brittle.
Modulus and tear strength of the nanocomposite increased up to 15 phr and then remained a constant up to 25 phr. There was only 11% increase in the modulus. Lack of strong interfacial bonding between nanokaolin and NBR matrix reduced the load transfer efficiency leading to the small improvement in modulus. The dispersed clay layers restricted the rubber chains and resisted the development of cracks, leading to an increase in tear strength.

Fig. 6.2. Variation of (A) Tensile strength/Elongation at break and (B) Modulus/Tear strength of the nanocomposite with clay ‘C’ loading.

6.3A.3 Strain sweep analysis

Fig. 6.3 shows the variation of complex modulus with strain % for uncured compounds containing different concentrations (0, 1, 5, 10, 15 phr) of nanokaolin. Complex modulus increased with increase in clay loading. At high concentration, the filler particles formed agglomerates leading to the formation of a filler network. This filler network resulted in the interaction of polymer chain with the filler particles leading to an increase in the complex modulus. At low strain the complex modulus would be high, but with the increase in strain destruction of network resulted in the reduction of complex modulus.
Fig. 6.3. Variation of complex modulus with strain for NBR-C nanocomposite

6.3A.4 Thermogravimetric analysis (TGA)

TGA thermograms of NBR and NBR containing 5phr and 15 phr nanokaolin are given in Fig.6.4 (A) and (B) respectively. DTG curve of NBR showed that degradation takes place in two steps with a shoulder at 428°C and a major peak at 456°C. This was due to the multiple degradation of the butadiene component present in raw rubber [1, 11, 12]. The degradation pattern of the nanocomposites also followed the same trend. Thermal degradation characteristic of NBR based nanocomposites are given in Table 6.2. The initiation temperature and the peak maxima showed a small increase by adding nanokaolin in NBR. Inclusion of an inorganic component to organic material improved the thermal stability [13]. High values of $T_{10}$, $T_{25}$ and $T_{50}$ showed increase in the thermal stability of the nanocomposite. Clay acted as an insulation and mass transport barrier against the volatile components produced during the thermal degradation of polymer [14]. Clay also formed a layered carbonaceous char during degradation of the nanocomposite and increased the thermal stability of the polymer [15].
Clay minerals are inorganic materials which are stable in the temperature range at which the polymer degrades and clay remains as residue after the heating programme [16].

Table 6.2. Thermal analysis results of NBR and NBR-C nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp.(°C)</th>
<th>Peak max.(°C)</th>
<th>Residue %</th>
<th>T_{10}(°C)</th>
<th>T_{25}(°C)</th>
<th>T_{50}(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>340</td>
<td>428, 456</td>
<td>6.783</td>
<td>376</td>
<td>420</td>
<td>445</td>
</tr>
<tr>
<td>NBR-5C</td>
<td>341</td>
<td>427, 455</td>
<td>15.45</td>
<td>379</td>
<td>423</td>
<td>449</td>
</tr>
<tr>
<td>NBR-15C</td>
<td>341</td>
<td>428, 458</td>
<td>16.69</td>
<td>380</td>
<td>425</td>
<td>452</td>
</tr>
</tbody>
</table>

Fig. 6.4. (A) DTG and (B) TGA curves of NBR and NBR-C nanocomposites

6.3A.5 Differential scanning calorimetry (DSC)

T_g of NBR and NBR-15 C nanocomposites are summarized in Table 6.3. T_g of NBR and its composite was almost the same, showing that the clay layers did not impose any restriction to the movement of polymer chains.

Usually, when polymer chain network gets adsorbed strongly on to the filler surface, effective degree of cross linking increases. The cross linking may be stronger if the filler contains some reactive surface groups that may cross...
link to the polymer chain. Either chemisorption or physisorption may take place at the filler surface. When chemisorption take place there will be permanent chemical bonding between filler particles and polymer chains. This severely restrict the movement of polymer chains relative to the filler surface, when high stresses are applied. While, physisorption arising from long range van der Waals forces between the surface of the filler and the polymer does not impose any hindrance to the chain mobility [17]. This might be the reason for the decrease in $T_g$ of NBR-C nanocomposite.

### Table 6.3. $T_g$ of NBR and NBR-15C nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>-22.71</td>
</tr>
<tr>
<td>NBR-15C</td>
<td>-23.91</td>
</tr>
</tbody>
</table>

#### 6.3A.6 X-ray diffraction analysis (XRD)

Fig.6.5 gives the typical X-ray diffraction patterns of nanokaolin and NBR/nanokaolin composite. The characteristic peaks of nanokaolin with spacing 7.05 ($2\theta=12.5^0$), 4.41 ($2\theta=20^0$) and 3.56 A$^0$ ($2\theta=25^0$) [18, 19] are shown in the figure. XRD peak at 12.5$^0$ corresponding to the interlayer space of 7.05A$^0$ was shifted to a lower angle in the nanocomposite, with a corresponding increase in the interlayer spacing. Shift to lower angle indicated intercalation of NBR into the clay galleries. The disappearance of the peaks between 13$^0$ and 25$^0$ in the nanocomposite showed exfoliation had taken place to some extent. Peak at a higher 20 value for the nanocomposite indicated collapse of some intercalated structure. Similar results were reported when montmorillonite was used as reinforcing filler. For NBR/sodium montmorillonite composite a peak appeared with a decrease in intensity compared to pristine Na-Mt [10]. S.Sadhu and Bhowmick, A. K.
have dealt with unmodified montmorillonite on SBR with varying styrene content and using dicumyl peroxide as the curing agent and suggested that exfoliation had taken place in all the nanocomposites.

![X-ray diffraction pattern of ‘C’and NBR-15C nanocomposite](image)

**Fig. 6.5. X-ray diffraction pattern of ‘C’and NBR-15C nanocomposite**

### 6.3A.7 Fourier transform infrared spectroscopy (FTIR)

Fig. 6.6. gives the IR spectrum of NBR and NBR-15C nanocomposite. The characteristic stretching vibration of nanokaolin, in the range 3600 cm⁻¹ was observed in the composite. The closely spaced peaks were due to the surface and inner hydroxyl groups in nanokaolin. The peaks at 2916 cm⁻¹ and 2844 cm⁻¹ due to CH stretching vibration of CH₂ groups of NBR remained with the same intensity in the nanocomposite. The peak at 2237 cm⁻¹ characteristic of CN group in NBR had no change in the nanocomposite, showing CN group had not involved in any chemical reaction. The strong peak at 1535 cm⁻¹ due to the presence of zinc stearate and the small peak at 1735 cm⁻¹ attributed to the CO stretching of the carboxyl group of zinc stearate were seen in the nanocomposite also. The difference in the IR spectrum of NBR and its nanokaolin composite lies in the range 1400-700 cm⁻¹. The CH₂ stretch vibration at 1256 cm⁻¹ had become
sharper in the nanocomposite. New peaks seen at 1094 cm\(^{-1}\), 1023 cm\(^{-1}\) and 913 cm\(^{-1}\) correspond to the stretching and bending vibrations of Si-O-Si and Al-OH groups in nanokaolin. The introduction of these sharp peaks in the nanocomposite showed there was strong interaction between the Si-OH and Al-OH groups in nanokaolin with the butadiene double bonds in NBR.

![IR spectrum of NBR and NBR-15C nanocomposite](image)

**Fig.6.6. IR spectrum of NBR and NBR-15C nanocomposite**

### 6.3A.8 Scanning electron microscopy (SEM)

Fig. 6.7(A) and (B) shows the SEM photographs of the tear fractured surface of NBR-C nanocomposite containing 15 phr nanokaolin. A uniform dispersion of clay particles were seen in the SEM images. Most of the clay particles were well embedded in the polymer matrix. This strong adhesion and good dispersion of clay particles in NBR matrix contributed to the reinforcing property of nanokaolin in NBR matrix.
6.3A.9 Conclusions

NBR nanokaolin composite showed good improvement in mechanical properties compared to the gum. Uniform dispersion of nanokaolin and the interaction of the OH groups of clay with the polar nitrile rubber led to the enhancement in mechanical properties of the nanocomposite. TGA studies showed that there was an increase in the thermal stability of the nanocomposite. The decrease in $T_g$ of the nanocomposite was an indication that the chain mobility is unaffected by the presence of clay. XRD results showed the intercalation of polymer into the intergallery space of clay. Analysis of the IR spectrum showed that there was only strong interaction between the Si-OH and Al-OH groups in nanokaolin with the double bonds in NBR.

6.3B. VinylSilane Grafted Nanokaolin in NBR

Silane treated clays are used as reinforcing fillers in natural and synthetic rubbers. The functional silanes usually employed for modification are vinyl or sulphur functional silanes. Vinyl functional silane treated clays are used in elastomeric applications where good compression set is required. This part deals with the study of the effect of vinylsilane grafted nanokaolin (V) in NBR. This modified nanokaolin gave good reinforcement in
properties when incorporated in NBR. The nanocomposites formed were characterized and their reinforcing effect was studied.

6.3B.1 Curing studies

Fig 6.8 shows the cure graphs of the compounds and the cure parameters are presented in Table 6.4. The addition of vinylsilane grafted nanokaolin retarded curing, as indicated by the increase in scorch time and optimum cure time and by decrease in CRI. Removal of some accelerator free radicals, formed by the interaction of the modified silicate with accelerator, during the cross linking reaction, retarded the curing reaction [2, 21]. Increase in $M_H$ and $\Delta M$ value gave the extent of cross linking reaction and the strong influence of the organoclay on the cross linking density of the rubber compound. The unsaturated sites of vinyl group gets cross linked with butadiene part of NBR in the vulcanization process. Moreover the polar low molecular mass vulcanization curatives like ZnO, ZDC, stearic acid and sulphur might easily penetrated between the clay layers resulting in rubber cross linking inside the clay galleries [21].

Table 6.4. Cure properties of NBR-V nanocomposites

<table>
<thead>
<tr>
<th>Concentration of ‘V’ (phr)</th>
<th>MinTorque $M_L$ (dNm)</th>
<th>MaxTorque $M_H$ (dNm)</th>
<th>$\Delta M = M_H - M_L$ (dNm)</th>
<th>Opt.cure time $T_{90}$ (min)</th>
<th>Sorch time $T_{10}$ (min)</th>
<th>Cure Rate</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.160</td>
<td>2.673</td>
<td>2.513</td>
<td>1.30</td>
<td>0.498</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.098</td>
<td>3.455</td>
<td>3.357</td>
<td>3.05</td>
<td>1.44</td>
<td>58.14</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.088</td>
<td>3.351</td>
<td>3.263</td>
<td>3.35</td>
<td>1.39</td>
<td>60.60</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.09</td>
<td>3.540</td>
<td>3.45</td>
<td>2.96</td>
<td>1.42</td>
<td>58.48</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.088</td>
<td>3.425</td>
<td>3.337</td>
<td>2.99</td>
<td>1.19</td>
<td>56.18</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.124</td>
<td>3.680</td>
<td>3.556</td>
<td>3.13</td>
<td>1.42</td>
<td>58.48</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.104</td>
<td>3.729</td>
<td>3.625</td>
<td>2.99</td>
<td>1.38</td>
<td>62.11</td>
<td></td>
</tr>
</tbody>
</table>
6.3B.2 Mechanical Properties

Mechanical properties of the nanocomposites are shown in Fig. 6.9 (A) and (B). From Fig 6.9 (A) it is clear the tensile strength and elongation at break of the nanocomposite increased with the clay loading upto 5 phr and then decreased. Tensile strength increased by 32% and elongation at break by 13%. Since tensile strength and elongation are properties that correlate with the interfacial phase adhesion it can be concluded that there was uniform dispersion and strong interfacial adhesion between the dispersed clay and polymer matrix.

Fig 6.9. Variation of (A) Tensile strength/Elongation at break and (B) Modulus/Tear strength of the nanocomposite with clay (V) loading
Modulus and tear strength increased with concentration of vinylsilane grafted nanokaolin as shown in Fig.6.9 (B). At 15 phr there was 24% increase in modulus and 33% increase in tear strength. The high shear stress generated during compounding helped in the delamination of the layered clays and the intercalation of rubber molecules into the gallery space.

6.3B.3 Strain sweep analysis

Fig.6.10. shows the variation in complex modulus with the addition of vinyl grafted nanokaolin (1, 5, 10 and 15 phr) in NBR. At low strain the complex modulus values of the nanocomposites was very high. But with increase in strain, complex modulus decreased. Formation of filler networks, i.e., either filler-filler or filler-polymer networks leads to the increase in complex modulus at low strain. In NBR-V nanocomposites, increase in complex modulus might be due to the interaction of polymer chains with the organic groups present in vinyl grafted nanokaolin. Destruction of network structure at high strain resulted in the decrease in complex modulus.

![Fig. 6.10. Variation of complex modulus with strain for NBR-V nanocomposite](image-url)
6.3B.4 Thermogravimetric analysis (TGA)

The thermal properties of NBR-V nanocomposites were studied by thermogravimetric analysis. Table 6.5 shows the thermal degradation data for NBR and NBR containing 7 phr and 15 phr modified nanokaolin (V). The TGA and DTG curves of pure NBR and the composites are shown in Fig. 6.11 (A) & (B). The DTG curves showed multiple degradation steps in nitrogen atmosphere [1]. Onset of degradation started around 340°C for all the vulcanizates. Hence the samples might be considered thermally stable up to 340°C in nitrogen atmosphere. There was slight increase in peak max. T2, T25 and T50. So the thermal stability of the nanocomposites increased by the addition of modified nanokaolin. The improvement in the thermal stability was due to the presence of intercalated/exfoliated clay layers. The hydrogen bonding interaction between the polar polymer chains with the OH groups of clay, along with vander Waals interaction improved the thermal stability of the nanocomposite. Alex and Nah [22] reported the thermal degradation temperature of NR/organoclay nanocomposite was independent of the presence and concentration of organoclay.

![Fig. 6.11 (A) TGA and (B) DTG curves of NBR and NBR-V nanocomposites](image-url)
It was also observed that the amount of residue increased with the increase in clay content. The residual materials were mainly due to zinc salts and inorganic fillers.

Table 6.5. Thermal analysis results of NBR and NBR-V nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp. (°C)</th>
<th>Peak max. (°C)</th>
<th>Residue %</th>
<th>T25 (°C)</th>
<th>T50 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T1</td>
<td>T2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBR</td>
<td>340</td>
<td>428</td>
<td>456</td>
<td>6.78</td>
<td>420</td>
</tr>
<tr>
<td>NBR 7V</td>
<td>339</td>
<td>427</td>
<td>456</td>
<td>12.98</td>
<td>422.44</td>
</tr>
<tr>
<td>NBR 15V</td>
<td>340</td>
<td>427</td>
<td>458</td>
<td>16.23</td>
<td>422.87</td>
</tr>
</tbody>
</table>

6.3B.5 Differential scanning calorimetry (DSC)

Table 6.6. gives the glass transition temperature (Tg) of NBR and NBR-V nanocomposite. The addition of modified clay did not produce any change in Tg indicating there was no restriction to polymer chain mobility. The interaction between the filler and polymer was only physisorption as against to chemisorption. Both physisorption and chemisorption leads to reinforcement in properties but the absence of chemical bond between the filler and polymer surface did not pose any restriction to the polymer chain mobility.

Table 6.6. Tg of NBR and NBR-15V nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>-22.71</td>
</tr>
<tr>
<td>NBR-15V</td>
<td>-23.23</td>
</tr>
</tbody>
</table>

6.3B.6 X-ray diffraction analysis (XRD)

Fig. 6.12 shows the XRD pattern of ‘V’ and NBR-15V nanocomposite. The peak corresponding to the interlayer spacing 7.1 Å in vinylgrafted
nanokaolin was slightly shifted to a smaller angle making a very small increase in the inter layer spacing. This showed the intercalation of rubber molecules into the inter layer space of the vinyl grafted moieties. Other characteristic diffraction peak of ‘V’ between 20, 20°-25° was absent in the nanocomposite. This showed the special directional and parallel arrangement of clay platelets in the rubber matrix. The SEM images (Fig.6.14) also confirmed the particular arrangement of the clay platelets.

On grafting silanes react mainly with some of the OH groups on the edge surface. Then only the lateral surface of clay particles will be organophilized. So there will not be any clay exfoliation in the presence of polymer and it will even be less effective than intercalation by ion exchange [21].

Fig. 6.12. X-ray diffraction pattern of V and NBR-15V nanocomposite

6.3B.7 Fourier transform infrared spectroscopy (FTIR)

Fig.6.13 shows the IR spectrum of NBR and NBR-15V nanocomposite. IR spectrum for unfilled and clay filled specimens did not show a significant difference in the range 3000-1500cm⁻¹. So there seemed to be no change in the
chemical arrangement. The peaks due to the OH groups (the closely spaced peaks around 3600 cm\(^{-1}\)) in nanokaolin were very much reduced (IR of vinylgrafted nanokaolin, Fig.3.6) in the nanocomposite. Peak at 1535cm\(^{-1}\) showing the presence of zinc stearate and the small peak at 1731 showing CO stretch of carboxyl group of zinc stearate were seen in NBR as well as NBR-V nanocomposite. The peak at 1463cm\(^{-1}\) in the nanocomposite might be formed by the merging of - CH\(_2\) - groups of NBR and vinyl group of modified clay. The peaks at 1103cm\(^{-1}\) and 1031cm\(^{-1}\) gave the perpendicular Si-O vibrations and Si-O-Si stretching vibrations respectively of the modified clay. The intensity of the peak at 968 cm\(^{-1}\) due to the butadiene double bond of NBR was reduced in the composite. This might be due to the interaction of butadiene double bond with the vinyl group of clay.

Fig. 6.13. FTIR of NBR and NBR-15 Vnanocomposite
6.3B.8 Scanning electron microscopy (SEM)

Fig.6.14 shows the SEM images of NBR-V nanocomposite under different magnification. Directional and parallel arrangement of clay platelets are seen in the SEM images.

Fig.6.14. SEM images of tear fractured surface of NBR-15 Vnanocomposite

6.3B.9 Conclusions

Good dispersion of modified clay in NBR resulted in the improvement in mechanical properties of the nanocomposite. Tensile strength increased by 32% and elongation at break by 13% at 5phr concentration. Modulus and tear strength of the nanocomposite increased with increase in the concentration of the filler. Modified clay got a cure retardation effect in NBR. Thermal analysis showed a slight increase in the thermal stability and no change in the glass transition temperature of the nanocomposite. Grafting with vinyl silanes caused organophilization only to the lateral surface of clay and so a complete exfoliation could not be expected in the presence of...
the polymer. IR analysis confirmed interaction of the vinyl group of clay with the buadiene double bond of the polymer chain. SEM photographs revealed the directional and parallel arrangement of the clay layers in NBR matrix.

6.3C. MWCNT in NBR

Carbon nanotubes show properties of both diamond and graphite. They are strong and thermally conductive like diamond, electrically conductive like graphite and also they are light and flexible [22]. In spite of the exceptional, thermal, electrical and mechanical properties of carbon nanotubes the expected reinforcement is not usually obtained by their incorporation in polymeric matrices. Nanotubes when mixed in rubber usually results in poor dispersion due to the attractive vander Waals bonds between the outer planes of neighbouring nanotubes resulting in their agglomeration [23]. Proper dispersion and distribution of these anisotropic filler is a challenging task. Dispersing nanotubes in polymer matrices can be achieved either by the formation of covalent bonds or by the establishment of a non covalent interaction between the polymer chain and nanotube surface [24]. Covalent modification involves reactive coupling between the functional moieties on the CNT surface with the available functional groups of the polymer. This significantly improves the structural properties of the nanocomposites. But studies have shown that covalent modification can perturb the extended $\pi$ conjugation system of CNT and adversely affect the intrinsic electronic characteristics of the nanotubes [25]. Noncovalent treatment is characterized by the adsorption of different hierarchical structures on the nanotube surface through various specific interactions. This method preserves the integrity of nanotubes, gives significant improvement
in the structural properties of the composite and shows a positive influence on the electrical conductivity of the nanocomposite [25].

Here the as received carbon nanotubes were first purified by refluxing with 500ml 2M HCl for 24 hours. This resulted in the introduction of hydroxyl and carbonyl groups on the surface of nanotubes, caused by the elimination of metallic nanoparticles during the purification process, cutting the nanotube caps [26, 27]. The purified nanotubes were incorporated in NBR, in very low concentrations. The composites were characterized and their mechanical, thermal and electrical properties were studied.

6.3C.1 Curing Studies

Cure parameters obtained during the curing process are reported in Table 6.7. Minimum torque is a measure of viscosity of the compound. The increase in minimum torque on the addition of MWCNT indicated an increase in viscosity and a reduction in the mobility of rubber chains [28]. The highest value of minimum torque was obtained at 0.3 phr MWCNT concentration. This is because at higher concentration occlusion of rubber takes place within and between the filler aggregates. This increased the immobility of the elastomer layers and thus led to an increase in the minimum torque value.

Maximum torque of the nanocomposites was very close to that of gum. Maximum torque is a measure of the extent of cross linking between the rubber chains and it gives the extent of filler polymer interaction. The very small concentration of MWCNT used might be insufficient to produce a considerable change in the torque value.
Scorch time is a measure of premature vulcanization or scorch safety of the rubber compound. Scorch time decreased with the addition of MWCNT. Similar behaviour was reported when MWCNT was added to NR [29]. Addition of thermally conducting MWCNT could improve the conductivity of NBR and thus help in vulcanization. Cure time which is the time required to reach maximum torque also decreased slightly with filler loading. Thus MWCNT had an accelerating effect on the cure reaction.

Cure rate index is a measure of rate of cure reaction. The rate of cure reaction increased initially and then decreased. Increase in cure rate index at low concentration might be due to the presence of crosslinks formed between MWCNT and NBR. When concentration of MWCNT increased the cross links were reduced due to agglomeration of MWCNT.

Table 6.7. Cure characteristics of NBR- MWCNT nanocomposite

<table>
<thead>
<tr>
<th>MWCNT loading</th>
<th>Min Torque M_L (dNm)</th>
<th>Max Torque M_H (dNm)</th>
<th>ΔM=M_H-M_L (dNm)</th>
<th>Opt. cure T_90 (min)</th>
<th>Scorch time T_10 (min)</th>
<th>Cure Rate Index CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.160</td>
<td>2.673</td>
<td>2.513</td>
<td>1.30</td>
<td>0.49</td>
<td>124</td>
</tr>
<tr>
<td>0.02</td>
<td>0.425</td>
<td>2.644</td>
<td>2.475</td>
<td>1.03</td>
<td>0.293</td>
<td>125.156</td>
</tr>
<tr>
<td>0.05</td>
<td>0.222</td>
<td>2.697</td>
<td>2.219</td>
<td>1.18</td>
<td>0.381</td>
<td>135.685</td>
</tr>
<tr>
<td>0.15</td>
<td>0.849</td>
<td>2.494</td>
<td>1.645</td>
<td>1.07</td>
<td>0.213</td>
<td>116.686</td>
</tr>
<tr>
<td>0.3</td>
<td>1.121</td>
<td>2.869</td>
<td>1.748</td>
<td>1.11</td>
<td>0.199</td>
<td>110</td>
</tr>
</tbody>
</table>

6.3C.2 Mechanical Properties

Fig.6.15(A) and (B) shows the variation of tensile strength/elongation at break and modulus/tear strength respectively of NBR-MWCNT nanocomposites. Tensile strength increased by 36% (0.05phr), modulus by 24% (0.3phr) and tear strength by 32% (0.02phr). After attaining an optimum value the mechanical properties decreased with higher loading.
A.M. Shanmugharaj et al. [30] have reported that the increase in tensile strength and modulus in polymer multiwalled carbon nanotube composites were not remarkable due to poor adhesion and weak van der Waals forces, which gave rise to lower stress transfer ability in the composites. But here even with a very low concentration of MWCNT there was considerable increase in tensile strength, modulus at 300% elongation and tear strength. This might be due to the interfacial bonding between the polar NBR matrix and the functional groups loaded on the surface of MWCNT during purification. Elongation at break of the nanocomposite decreased with the incorporation of MWCNT. Cracks are usually initiated at the in-homogenities like voids, and nanotube agglomerates act as stress concentrators or weak spots of cross link density [23]. So the decrease in elongation might be attributed to an insufficient dispersion of CNT agglomerates.

[Fig 6.15. Variation of (A) tensile strength and elongation at break (B) modulus and tear strength of NBR-MWCNT nanocomposites]

6.3C.3 Swelling studies

Swelling studies of the vulcanizates containing different concentration of MWCNT were done in MEK at room temperature. Fig.6.16 shows the decrease in swelling index with the addition of MWCNT. As the filler loading increased
the solvent uptake decreased due to the increased hinderance exerted by nanotubes at higher loadings. Contribution to reinforcement effect arose from molecular interaction between rubber and filler. This interaction led to an increase in the effective degree of cross linking and could be evaluated from equilibrium swelling. As the cross linking increased the swelling ratio decreased.

The entangled structure of nanotubes having nanometer scale diameters and micrometer scale lengths can themselves provide physical cross links. This will result in more cross link in the composite than in unfilled NBR, eventhough the chances for a chemical reaction between MWCNT and NBR are negligible.

Sorption curves of the vulcanizate were obtained by plotting Qt % against time as given in Fig.6 17. The uptake of the solvent was rapid initially but soon reached an equilibrium state. The unfilled vulcanizate had the maximum uptake at equilibrium swelling. The curves showed two distinct regions-an initial steeper region with high sorption rates due to large concentration gradient and a second region exhibiting reduced sorption rates that ultimately reached equilibrium. The value decreased with increase in filler loading.
6.3C.4 Thermogravimetric analysis (TGA)

The thermal behaviour at the heating range of 30°C to 700°C of the neat polymer and the MWCNT filled samples are shown in Fig.6.18. (A) and (B). Thermal analysis data is given in Table 6.8. Due to the multiple degradation steps of the butadiene component present in raw rubber, unfilled NBR degraded in two steps with one minor peak at 428°C and a major peak at 456°C. The nanocomposite also followed the same pattern. Temperature at 10%, 25% and 50% weight losses for the nanocomposite were the same as that of gum. Peak maxima were also, almost the same. So the inclusion of nanotube in such a small concentration did not affect the thermal stability of the nanocomposite.

**Fig 6.18 (A) DTG and (B) TGA curves of NBR and NBR 0.05MWCNT**

**Table 6.8.Thermal analysis results of NBR and NBR-0.05 MWCNT**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp. (°C)</th>
<th>Peak max.(°C)</th>
<th>Residue %</th>
<th>T_{10} (min)</th>
<th>T_{25} (min)</th>
<th>T_{50} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>340</td>
<td>428</td>
<td>456</td>
<td>6.783</td>
<td>375</td>
<td>420</td>
</tr>
<tr>
<td>NBR-0.05 MWCNT</td>
<td>334.31</td>
<td>425.31</td>
<td>456.58</td>
<td>11.22</td>
<td>375.51</td>
<td>420.98</td>
</tr>
</tbody>
</table>
6.3C.5 Differential scanning calorimetry (DSC)

The glass transition temperatures of NBR and NBR-MWCNT nanocomposites are given in Table 6.9. In conventional composites due to the interaction between filler and rubber molecules the molecular motion of rubber molecules will be affected and the influence can be reflected in thermoanalysis curve. Loss in mobility of the chain would result in an increase in $T_g$ and most probably in a change of the thermal expansion of the free volume. Here it is believed that the amount of carbon nanotubes used were too small to produce any change in the chain flexibility/$T_g$

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>-22.57</td>
</tr>
<tr>
<td>NBR-0.05 MWCNT</td>
<td>-22.57</td>
</tr>
<tr>
<td>NBR-0.3 MWCNT</td>
<td>-23.42</td>
</tr>
</tbody>
</table>

6.3C.6 X-ray diffraction analysis (XRD)

Fig.6.19 shows the XRD diffractograms of MWCNT, NBR and NBR-MWCNT nanocomposite. The characteristic peak of MWCNT is at 25.7$^\circ$. The nanocomposite did not show any peak in this range. This showed the absence of an ordered intercalated or rather an exfoliated structure of the nanocomposite.
Fig. 6.19. X-ray diffraction pattern of MWCNT, NBR and NBR-0.05MWCNT

6.3C.7 Fourier transform infrared spectroscopy (FTIR)

Fig. 6.20 shows the IR spectrum of NBR and NBR-0.05MWCNT nanocomposite. The increase in the intensity of the band at 969 cm\(^{-1}\) confirmed the interaction of the \(\pi\) electrons of the nanotube with the butadiene double bond. The introduction of the peak at 1594 cm\(^{-1}\) might be due to C=C from the MWCNT. The increase in the intensity of the band at 2235 cm\(^{-1}\) might be due to the polar interaction of the carboxylic group of nanotube with the CN group of NBR.

Fig. 6.20. FTIR spectrum of NBR and NBR-0.05MWCNT nanocomposite
6.3C.8 Scanning electron microscopy (SEM)

SEM images of the tear fractured surface of the nanocomposite are shown in Fig. 6.21. The rough surface of the nanocomposite showed typical brittle fracture behaviour with a lot of agglomerates. It seemed that the nanotubes having weak interface are pulled out of the matrix showing that the interfacial bonding between the CNTs and the rubber matrix need to be improved.

![SEM image of NBR-0.05 MWCNT nanocomposite]

**Fig. 6.21.** SEM images of NBR -0.05 MWCNT nanocomposite

6.3C.9 Conductivity

The electrical conductivity of polymer nanocomposite with carbon nanotubes depend on several factors, like nanotube concentration, polymer matrix, filler-matrix interaction, filler orientation and the processing techniques intended to improve the dispersion of carbon nanotubes in the host matrix [31].

In general, the electrical conductivity of a particulate composite reveals a non-linear increase with the filler concentration, passing through a percolation threshold, as shown in Fig.6.22. At low filler concentrations, the conductive particles are separated from each other and the electrical
properties of the nanocomposite are dominated by the matrix. With increasing filler concentration local clusters of particles are formed. At the percolation threshold, these clusters form a connected three-dimensional network through the component, resulting in a jump in the electrical conductivity.

![Graph showing electrical conductivity of NBR/MWCNT nanocomposites](image)

**Fig. 6.22. Electrical conductivity of NBR/MWCNT nanocomposites**

### 6.3C10 Conclusions

Purification of MWCNT by refluxing with HCl introduced OH and CO groups in it. Mechanical properties of NBR increased with the addition of MWCNT. Presence of nanotube restricted the solvent swelling capacity of the nanocomposite. There were no appreciable changes in the thermal stability and glass transition temperature of the nanocomposites. IR spectrum confirmed the absence of a chemical bond between NBR and MWCNT. SEM images showed pull out of MWCNT which might be due to the poor interaction of MWCNT in NBR. MWCNTs increased electrical conductivity of NBR.
6.3D Graphene Nanoplateles in NBR

Graphene nanoplatelets were incorporated in NBR at very low concentration. Cure characteristics, mechanical and thermal properties of the nanocomposites were studied. They were further characterized by XRD, FTIR and SEM analysis.

6.3D.1Curing studies

The cure characteristics of graphene loaded NBR is given in Table 6.10. Minimum torque of the nanocomposite was almost equal to that of gum. The addition of graphene in small concentration did not affect the viscosity or mobility of rubber chains. Certain nanostructures when dispersed in various polymers can form network structures that could constrain the motion of polymer chains. Another reason for the low viscosity might be the lubricant property of graphene [32].

Maximum torque $M_H$ and $\Delta M$ ($M_H-M_L$) showed a slight increase on the addition of graphene. The increase in $M_H$ and $\Delta M$ are usually the effect of an increase in cross link density. Here the physical interaction of the graphene platelets with NBR and the wrinkled topology of graphene platelets would have enhanced mechanical locking and adhesion and have slightly accelerated the curing reaction.

A small increase in modulus (6%) of the nanocomposite also indicated the reinforcement is not due to the increase in cross linking, but it is an effect of the physical interaction and nanofiller geometry [33]. Optimum cure time i.e. the time taken for obtaining 90% of the maximum torque was almost a constant and there was increase in the scorch time showing a better processing safety for the nanocomposite.
inclusion of graphene increased the rate of curing reaction by participating in the cure reaction as observed by the increase in the CRI value.

### Table 6.10. Cure characteristics of NBR/ graphene nanocomposite

<table>
<thead>
<tr>
<th>Graphene Loading (phr)</th>
<th>Min. Torque $M_L$ (dNm)</th>
<th>Max. Torque $M_H$ (dNm)</th>
<th>$\Delta M = M_H - M_L$</th>
<th>Opt. cure $T_{90}$ (min)</th>
<th>Scorch time $T_{10}$ (min)</th>
<th>Cure Rate Index CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.160</td>
<td>2.673</td>
<td>2.513</td>
<td>1.30</td>
<td>0.49</td>
<td>124</td>
</tr>
<tr>
<td>0.05</td>
<td>0.167</td>
<td>3.040</td>
<td>2.873</td>
<td>1.34</td>
<td>0.69</td>
<td>153</td>
</tr>
<tr>
<td>0.15</td>
<td>0.160</td>
<td>2.954</td>
<td>2.794</td>
<td>1.32</td>
<td>0.60</td>
<td>138</td>
</tr>
<tr>
<td>0.3</td>
<td>0.157</td>
<td>2.899</td>
<td>2.742</td>
<td>1.25</td>
<td>0.56</td>
<td>147</td>
</tr>
</tbody>
</table>

#### 6.3D.2 Mechanical properties

The variation in mechanical properties of graphene filled NBR are given in Fig 6.23 (A) and (B). The addition of graphene platelets showed marked increase in tensile strength and elongation at break. The addition of 0.3 phr graphene increased the tensile strength to 162% and elongation at break to 47%.

The intrinsic properties of graphene, their wrinkled structure and the physical interaction with the host polymer might have enhanced the mechanical interlocking and adhesion of graphene to the polymer matrix. This strengthened the interaction and load transfer between graphene and NBR leading to reinforcement in properties [33,34].

The dispersed graphene platelets with the wavy and wrinkled structure would unfold rather than stretch inplane under an applied tensile stress leading to a small increase in modulus (6%) and tear strength (16%).
Incomplete exfoliation and restacking of platelets also led to lowering of modulus values due to decreased aspect ratios [34].

![Graph](image)

**Fig 6.23. Variation of (A) Tensile strength and Elongation at break (B) Modulus and Tear strength of the NBR-graphene nanocomposite**

### 6.3D.3 Swelling studies

Fig.6.24. shows the plot of MEK uptake, Qt mole (%) against time, of graphene reinforced NBR. On the addition of graphene, swelling rate showed a rapid decrease. All the samples showed regular increase in swelling with time. The rate of uptake increased at first, but later became constant as final equilibrium is approached. These curves are often referred to as sigmoid sorption curves [35]. At 0.05 phr graphene concentration swelling was least and cross link density maximum. Fig. 6.25 gives the variation of swelling index with concentration of graphene. As the filler concentration increased the solvent uptake decreased.
6.3D.4 Thermogravimetric analysis (TGA)

Fig.6.26 (A) and (B) gives the DTG and TGA curves of non-oxidative thermal degradation (under nitrogen flow) of NBR and NBR containing 0.15 phr graphene. Their thermal stability data is given in Table 6.11. It is seen that very low concentration of graphene did not affect the thermal stability of the nanocomposite. There was no change in the onset degradation temperature, peak maximum, temperature at 10%, 25%, and 50% weight loss for the nanocomposite.

Fig.6.26 (A) DTG and (B) TGA curves of NBR and NBR-0.15 graphene
Table 6.11. Thermal analysis results of NBR and NBR-0.15 graphene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temp. (°C)</th>
<th>Peak max.(°C)</th>
<th>Residue %</th>
<th>T10 (min)</th>
<th>T25 (min)</th>
<th>T50 (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>340.6</td>
<td>428.49</td>
<td>455.91</td>
<td>6.783</td>
<td>375.60</td>
<td>420.24</td>
</tr>
<tr>
<td>0.15G</td>
<td>341.2</td>
<td>427.75</td>
<td>455.56</td>
<td>5.873</td>
<td>374.78</td>
<td>419.67</td>
</tr>
</tbody>
</table>

6.3D.5 Differential scanning calorimetry (DSC)

Table 6.12 gives the glass transition temperature of NBR and NBR-graphene nanocomposites. At 0.05 and 0.15 phr concentration of graphene, there was no change in the glass transition temperature. But when concentration was increased to 0.3phr, a slight increase in Tg was observed. Thus the mobility of NBR chain was restricted when the concentration of graphene platelets increased.

Table 6.12. Tg values of NBR and NBR-0.15 graphene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>-22.57</td>
</tr>
<tr>
<td>NBR-0.05 Graphene</td>
<td>-23.07</td>
</tr>
<tr>
<td>NBR-0.15 Graphene</td>
<td>-22.37</td>
</tr>
<tr>
<td>NBR-0.3 Graphene</td>
<td>-21.57</td>
</tr>
</tbody>
</table>

6.3D.6 X-ray diffraction analysis (XRD)

Like nanoclays graphene also has a layered structure, so when dispersed in a polymer matrix graphene exhibits similar states of dispersion like stacked, intercalated or exfoliated depending on their processing techniques and affinity between the plates. Fig.6.27 gives the XRD diffractograms of graphene, NBR and NBR-0.15 graphene nanocomposite.
in the 2θ range 0-30°. The characteristic broad peak of graphene was found at 2θ 0. The composite was devoid of any peaks in this 2θ range. So the polymer molecules must have exfoliated the graphene layers.

![X-ray diffraction pattern of graphene, NBR and NBR-0.15 graphene](image)

**Fig. 6.27. X-ray diffraction pattern of graphene, NBR and NBR-0.15 graphene**

**6.3D.7 Fourier transform infrared spectroscopy (FTIR)**

Fig. 6.28 shows the IR spectrum of NBR and NBR-0.15 graphene. The peaks in the range 2900 and 2850 cm⁻¹ attributed to the CH stretch vibration are seen in the unfilled and filled polymer. The characteristic peak of CN remained intact in the nanocomposite, showing there is no interaction of graphene platelets with the CN group of NBR. The peak in the range 1530 cm⁻¹, representing the zinc carboxylate ion was seen in the composite also. The butadiene stretch at 969 cm⁻¹ had become sharper and intense. This might be due to the interaction of butadiene double bond with the pi electrons of graphene. The peaks due to CH₂ deformation at 1452, 1397 and 1262 cm⁻¹ have reduced in the composite. So from the IR spectra it can be inferred that in the composite there is only interaction of CH₂ groups and pi electrons of graphene with the butadiene double bond of NBR.
6.3D.8 Scanning electron microscopy (SEM)

Fig 6.29 gives the SEM images of NBR-graphene nanocomposites. Graphene platelets do not appear flat, but have a curved wrinkled structure. This structure might be due to the intrinsic flexibility of the atomically thin sheets. This structure helped in the dispersion of the graphene platelets and minimized restacking of the platelets. The graphene platelets seemed to be well embedded in the polymeric matrix showing the adhesion of the filler with the matrix.
6.3D.9 Conclusions

NBR/graphene nanoplatelet composites prepared by the simple mill mixing method had shown good improvement in tensile strength and elongation at break. Thermal stability of the nanocomposite was unaffected by the incorporation of a small amount of graphene. There was a small improvement in the glass transition temperature of the nanocomposite at a higher concentration. XRD analysis showed the exfoliation of graphene layers in the nanocomposite. From IR spectrum it was clear that there was no chemical bonding between graphene platelets and NBR.
References


