Chapter V

Results and Discussion – NBR Polymer Nanocomposites using DOP as dispersion aid
CHAPTER V : Acrylonitrile Butadiene Rubber Nanocomposites - Dop As Dispersion Aid

Introduction

In the recent years, polymer nano-clay composites turned out to be of great interest for researchers as they exhibit extraordinary properties which have many industrial applications. Materials with combination of nano-sized organic / inorganic materials and polymers expected to give the properties that are synergistic combinations of the individual components with the reinforcing components are mostly nano-clay, nano-silica, nano-graphite, carbon nano-tubes (CNT) etc. These are class of organic / inorganic hybrid materials, where the inorganic components are uniformly distributed in nanometer scale ($10^{-9}$ m) within the polymer matrix.

Elastomers were reinforced with fillers to improve their performance by incorporating conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate etc. The nano fillers with very small amount could reinforce the polymer matrix. The resulting polymer nano composites thus comprise nano fillers embedded in a polymerized medium that can be subsequently cross-linked, to obtain vulcanized rubber nanocomposites. Nano-composites made out of nano fillers had shown to afford remarkable property enhancements compared to conventional micro composites [1–3] that were made using conventional fillers. Polymer nano-composites with layered silicates [4–9] and carbon nano tubes [10–12] have attracted major interest for the improvement of structural a properties and the development of new materials having different functional properties. Nano-graphite is a layered material with high aspect ratio in its exfoliated state is also considered as one of the strongest materials per unit weight and has unique functional properties e.g. good electrical and thermal conductivities, and good lubricating properties. The crystal structures of clays are usually interesting in their own right. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of either aluminium or magnesium is fused to two external silica tetra hydrate by their tip so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. Acrylonitrile Butadiene Rubber (NBR)-Nanographite polymer nano composites were found to increase its thermal stability [13]. Mechanical and tribological properties of NBR filled with graphite and carbon black were studied. [14] Effects of Radiation on SBR-EPDM
Rubber based Carbon nanotubes composites were reported \cite{15}. SBR – nanoclay based nanocomposites were optimized using face centered central composite design \cite{16}.

In general, the degree of dispersion of the clay platelets into the polymer matrix determines the super structure of the nanocomposites. Depending on the interaction between the clay and the polymer matrix, two main idealized types of polymer-clay morphologies, intercalated and exfoliated, and a third less ideal flocculated morphology can be obtained (Fig.5.1). Flocculation is more readily found in suspensions of charged particles in low viscosity, low molecular weight liquids, in which edge-edge interactions are significant. The intercalated structure results from penetration of a few polymer chains into the silicate interlayers. Face-to-face attractions persist resulting in formation of alternate layers of polymer and inorganic layers. The platelets are exfoliated when the individual silicate layers are completely separated and dispersed randomly in a polymer matrix, where no electrostatic interactions between surfaces exist. The best property improvements in polymer composites and the least influence to viscosity for low molecular weight suspensions results from the exfoliated morphologies.

Since as of now also dispersion complexities of nano filler in to the rubber matrix has not been overcome due to its high surface area and energy, therefore in this work, we adopted a new technique to incorporate nanoclay in Acrylonitrile Butadiene Rubber (NBR) matrix using Dioctyl Phthalate [DOP] as dispersing media in order to obtain uniform dispersion. Since, DOP has been used as processing oil for rubber compounding and because of its liquid form it is convenient to disperse nanoparticles into this as compared to directly dispersing in to the rubber. The changes obtain in the morphology,

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.1.png}
\caption{Polymer –Fillers interaction}
\end{figure}
permeability, mechanical & dynamic mechanical analysis were studied. Dioctyl-Phthalate is still used on a widely spread base all around the world. For example as coating for pills or as nutritional supplement for several products. Also adhesives, medical devices, toys, modeling clay, paints, printing inks and coatings, waxes, pharmaceuticals, paints, contain the chemical. Almost every product made of soft plastic needs Dioctyl-Phthalate in order to make the material more flexible and smooth. Furthermore, it is not soluble in water, but in oil. The chemical is the result of the reaction between phthalic anhydride with an alcohol. at -50 °C it starts melting and boiling at 384 °C, under habitual conditions Dioctyl-Phthalate stable. If Dioctyl-Phthalate is mixed with plastic, it allows the huge polvinyl molecules to slide and creates a more dense packed material. Therefore, DOP has been a most important ingredient in rubber processing.

5.1 Conventional Mixing:

The compound was prepared as per the compounding formulation given in Table-1. Polymer nano compounds were prepared by mixing NBR and other compounding chemicals using a open two roll mixing mill operated at room temperature and the speed ratio of the two rolls were maintained at

5.2 Mixing with dispersed nano clay

The compound was prepared as per the compounding formulation given in Table-1. Polymer nano compounds were prepared by mixing Nano clay in DOP oil oil with the help of steering machine at the 1000 rpm and mixture of such pre-dispersed nanoclay was added to NBR and other compounding chemicals using a open two roll mixing mill operated at room temperature and the speed ratio of the two rolls were maintained at 1:1.2.

5.3 Permeability studies

The permeability studies were carried out in air permeability tester as per IS 3400 (Part 21). An absolute pressure in the range of 0.3 – 1.5 MPa was kept for high pressure side and low pressure side was maintained at the prevailing atmospheric pressure. The test samples are mechanically conditioned initially for 24 hrs, and permeability study was conducted at standard laboratory condition of 27 ± 1 °C test temperature.
5.4. Contact Angle Analysis

The CA analysis was done at 26-27 °C (the room temperature that time). Water didn’t leave any spot on the samples whereas diiodomethane (DIM) left a spot after study indicating DIM swells the supplied matrices.

5.4.1 Wet ability and surface energy analysis

Millipore-Q water (conductivity 0.05 μS.cm⁻¹) was used for contact angle studies. Dynamic contact angle analysis by wetting angle measurements was carried out. The mounted samples were placed on a glass plate and a drop of known volume of water was allowed to fall on the smooth surface of sample. The measurement of contact angles of the sample was carried out by sessile drop technique using image analysis software. A liquid droplet (1.5- 2.5 μl) was allowed to fall on the samples to be studied from a software-controlled syringe. An image sequence was taken through a CCD camera of goniometer from GBX instruments, France which was connected to a PC computer and interfaced to image capture software (Windrop⁺⁺, GBX instruments).

The Owens and Wendt method was used to determine the total surface energy and its resolution into polar and dispersive component [22], wherein the total solid surface tension γ was assumed to be of the general form as shown in equation (1)

\[
1 + \cos \theta = 2\sqrt{\gamma_s^d (\gamma_1^d/\gamma_1)} + 2\sqrt{\gamma_s^p (\gamma_1^p/\gamma_1)}
\]  

(1)

In this equation, the subscripts s and 1 refer to the solid and liquid surface tension respectively; the superscripts d and p coincide with dispersive and polar components of total surface tension, where sum of these two values are equal to the total surface tension. The \(\sqrt{\gamma_s^d}\) and \(\sqrt{\gamma_s^p}\) are needed to be resolved. Therefore two independent contact angles were measured by two different liquids (water and diiodomethane) whose surface tension components are known.
5.6. Rheological Properties

Rheological data of compounds were tabulated in Table 5.1 the rheograms showed that addition of nanoclay into the NBR matrix increased the torque. The rheograms for NBR nanocomposites obtained are shown in Table 2. Nanoclay dosage doesn’t affect much the curing time of the compound, since optimum cure time of the NBR nano compounds slightly increase in both the cases of dispersion of nanocalys. Various cure characteristics of NBR nanocomposites are summarized in Table 5.1. The possible formation of a MMT complex in which sulphur participation may facilitate for the increase in rate of cure.[17] From the study of the effect of nanoclay content on rheometric torque of NBR Nanocomposites.

<table>
<thead>
<tr>
<th>Curing properties</th>
<th>NBC0</th>
<th>NBC3</th>
<th>NBC5</th>
<th>NBC7</th>
<th>NBDC3</th>
<th>NBDC5</th>
<th>NBDC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum torque, Lbs</td>
<td>38.76</td>
<td>36.94</td>
<td>33.23</td>
<td>30.86</td>
<td>34.65</td>
<td>34.18</td>
<td>31.40</td>
</tr>
<tr>
<td>Minimum torque, Lbs</td>
<td>6.21</td>
<td>6.86</td>
<td>6.89</td>
<td>6.93</td>
<td>6.32</td>
<td>6.69</td>
<td>7.28</td>
</tr>
<tr>
<td>Optimum cure time T 90, minutes</td>
<td>4.08</td>
<td>3.99</td>
<td>4.06</td>
<td>4.09</td>
<td>4.33</td>
<td>4.12</td>
<td>4.11</td>
</tr>
</tbody>
</table>

minimum torque, an indirect measure of viscosity of the compound, marginally increased gradually as nanoclay content increases in both the cases, conventional mixing and DOP assisted mixing. The maximum torque depends on both the extent of crosslinking and reinforcement by the filler particles in the polymer matrix.

The difference between maximum and minimum torques, an indication of the extent of cross linking, was found to increase with filler loading. This may be due to the incorporation of NBR chains into the galleries of the nanoclay resulting in better interaction between the nanoclay and the rubber matrix. But, here, it is clearly noticeable
that there is similar characteristic exhibiting in case of DOP assisted dispersion of nanoclays however it is observed that in this case corresponding values of torque of DOP assisted dispersion was lesser compare with Directly dispersed nanoclays and this characteristics can attributed to the facts that de agglomeration and proper dispersion of nanoclays by DOP in the NBR lead to the lowering of maxim torque.

5.7. Mechanical Properties

5.7.1 Tensile strength

Tensile strength was increased with the dosage of Nanoclay in NBR compounds up to 5phr and then decreasing at 7 phr as shown in Fig.5.2, for composites prepared by dispersed mixing of nanoclay in DOP oil shown good improvement in Tensile strength compared to normal mixed compounds up to 3 phr. At 5 phr the values are same. As the Nanoclay varies from 5 to 7, the viscosity increased and a stage reached in which the dispersion is not so good and which results in as the de agglomeration. So the difference in properties of NBC & NBDC compounds decreased with the increase in phr after 5phr.

![Fig. 5.2 Tensile Strength of HNBR-clay nanocomposite with and without DOP assisted dispersion](image-url)
5.7.2 Tensile modulus

Table: 5.2 Tensile modulus of PNCs with different loading of nano clay in NBR matrix

<table>
<thead>
<tr>
<th>Modulus</th>
<th>NBC0</th>
<th>NBC3</th>
<th>NBC5</th>
<th>NBC7</th>
<th>NBDC3</th>
<th>NBDC5</th>
<th>NBDC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>11</td>
<td>15</td>
<td>19</td>
<td>21</td>
<td>12</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>200%</td>
<td>12</td>
<td>23</td>
<td>29</td>
<td>33</td>
<td>17</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td>300%</td>
<td>15</td>
<td>34</td>
<td>43</td>
<td>44</td>
<td>25</td>
<td>33</td>
<td>38</td>
</tr>
</tbody>
</table>

All tensile modulus properties were increased with increase in Nanoclay dosage due to the efficient reinforcement of nanoparticles up to 5 phr as shown in Table 5.2. The modulus of well dispersed nano clay compounds was better than normally mixed compounds up to 3 phr and almost comparable in 5 phr dosage. But after this NBC compounds shown better modulus than NBDC compounds due to the lack of dispersion.

5.7.3 Elongation @ break

The elongation @ break of pre-dispersed Nanoclay compounds gradually decreases with dosage (Fig.5.3) due to the increased reinforcement. But in the case of normally mixed samples the trend was same but it didn’t follow the regular reduction path compared to the pre-dispersed one. The values at 0,1 and 3 phr as well as the values at 5 and 7 phr were same for normally mixed compounds. This again proves the improper dispersion of nano clay in matrix.

![Elongation @ break of NBR-clay nano-composite with and without DOP assisted dispersion](image)
5.7.4 Hardness

Hardness is defined as the resistance to indentation. The durometer is an instrument that measures the penetration of a stress-loaded metal sphere into the rubber. As clear from the Fig.5.4. The resistance to indentation of PNCs were increasing with an increase of nano filler loading. This can be attributed to the fact that as in the normal dispersion also as the others test results like Tan delta shows that incorporation of nanoclays increase the stiffness of material and which enhances the compactness of the materials and leads to the increase in the hardness also.

Fig.5.4 Hardness of NBR with of HNBR-clay nanocomposite with and without DOP assisted dispersion

5.7.5 Tear strength

Tear strength of Nanoclay compounds increases with increase in dosage of Nanoclay up to 5 phr then remains the same. So we can optimize the dosage at 5phr (Fig.5.5).

Fig.5.5 Tear strength of NBR of -clay nanocomposite with and without DOP assisted dispersion.
This is mainly due to the better reinforcement of nanofiller in the NBR matrix. Compared to normally mixed compounds pre-dispersed compounds have good tear strength. At 3 phr we can see a 30% improvement in tear strength for pre dispersed compound due to the better dispersion of nano filler.

5.7.6 Air Permeability studies

The transport behaviour through composites depends on the type of filler, matrix, temperature, size of the penetrate, polymer segment mobility, reaction between solvent and the matrix, etc. Hence the study of the transport process through composites can be used as an effective tool to understand the interfacial interaction and morphology of the system.

Air permeability of Nanoclay compounds reduced with the addition of nanoclay in NBR up to 5 phr is appreciable and then decreased abruptly in 7 phr of HDN7, and the improvement up to 5 phr was due to the uniformly dispersed intercalated structure of nano clay and while increasing the dosage the interlayer spacing reduces and so the air permeability decreases. The impermeability was more observed in pre-dispersed compounds due to its better dispersion.

![Fig.5.6 Permeability of NBR clay nanocomposite with and without DOP assisted dispersion](image_url)
The decreased permeability of clay nano composite arises from the longer diffusion path that the penetrant must travel in the presence of clay nano-layers. Naturally, increasing nanoclay loading can provide longer diffusion path, and therefore improve gas barrier property. In this mechanism, Lu and Mai\cite{18} and Bharadwaj\cite{19} have shown that the filler aspect ratio (i.e., diameter/thickness for silicate layer) is a crucial factor. Since exfoliated clay layers have much larger aspect ratios than intercalated structures, they have better gas barrier property. It can also be concluded that the clay layers with the large aspect ratio and the planar orientation and better dispersion lead to the great increase of the diffusion distance by creating a tortuous path for the diffusing gas.

5.7.7 Contact Angle Analysis

Two set of samples NBDC series and NBC series for contact angle analysis were studied. As clear from the figure above for NBDC series addition of additive resulted in increase in initial and contact angle indicating the better dispersion of nanoclay causes it to become more hydrophobic. However there was not much difference in contact angle for NBDC3 and NBDC7 series indicating addition of different amount of additive did not affect the contact angle much.

![Contact Angle Study](image)

**Fig 5.7** Contact angle study NBR clay nanocomposite with and without DOP assisted

Sample code NC = NBC, NBRDNC = NBDC
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NBDC0 (0s)-Water

NBDC0 (156 ms)-Water

NBDC (0s)-Diiodomethane

NBDC0 (156 ms)-Diiodomethane

NBDC3 (0s)-Water

NBDC3 (156 ms)-Water

NBDC7 (0s)-Water

NBDC7 (156 ms)-Water
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NBDC (0 s)-Diiodomethane

NBDC0 (156 ms)-Diiodomethane

NBC1 (0 s)-Water

NBC1 (156 ms)-Water

NBC1 (0 s)-Diiodomethane

NBC1 (156 ms)-Diiodomethane

NBC 3 (0 s)-Water

NBC 3 (156 ms)-Water

NC 5 (0 s)-Water

NC 5 (156 s)-Water
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**Fig 5.8** Contact Angle Analysis

**Table 5.3** The properties of liquids used for surface energy determination

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface Tension (mN / m)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_1$</td>
<td>$\gamma_1^d$</td>
<td>$\gamma_1^p$</td>
</tr>
<tr>
<td>Water</td>
<td>68.9</td>
<td>18.6</td>
<td>50.3</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>49.7</td>
<td>48.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 5.4** Surface energy of samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface energy (mJ / m²)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Energy</td>
<td>Polar component</td>
<td>Dispersive component</td>
</tr>
<tr>
<td>NBDC0</td>
<td>30.4</td>
<td>4.7</td>
<td>25.7</td>
</tr>
<tr>
<td>NBDC3</td>
<td>34.6</td>
<td>6.6</td>
<td>28.0</td>
</tr>
<tr>
<td>NBDC7</td>
<td>30.2</td>
<td>3.7</td>
<td>26.5</td>
</tr>
<tr>
<td>NBC1</td>
<td>28.6</td>
<td>3.9</td>
<td>25.6</td>
</tr>
<tr>
<td>NBC3</td>
<td>28.8</td>
<td>2.5</td>
<td>26.3</td>
</tr>
<tr>
<td>NBC5</td>
<td>28.1</td>
<td>1.8</td>
<td>26.3</td>
</tr>
<tr>
<td>NBC7</td>
<td>26.6</td>
<td>3.0</td>
<td>23.6</td>
</tr>
</tbody>
</table>
NBC series showed slight increase and then decrease in CA at higher nanoclay content. In comparison with NBDC series the samples of NBC series showed higher contact angle (without the fillers) indicating control NBC sample is more hydrophobic than controlled NBDC sample.

Surface energy (SE) measurements indicated (Table.5.4) that there surface energy of NBC series was much lower than NBDC series. Also there was not much change in SE of NBC series on addition of nanoclays but NBDC series showed change in surface energy of the samples to some extent due to better dispersion.

5.7.8 Scanning Electron Microscopy

Figure-9 [a and b] shows scanning electron micrographs of tensile fracture surface of NBR Clay based polymer Nano-composites (NBC-for conventional mixing and NBDC - DOP assisted dispersion of Nano clay in to the NBR Matrix).The Figure-9 (a) shows the mapping of the NBR composite with 3 phr clay, Fig-9 (b) shows the dispersion of 5 phr of nanoclays by element dispersive spectrum of polymer nanocomposites by conventional method.
Fig. 5.9 (c & d) represent the DOP assisted dispersion of nanoclays filled NBR with 5 and 7 phr respectively, reveals that the particles were not aggregated much in Fig. (c & d) compare with fig.( b & c). Even at the 7 phr nanoclays incorporation in DOP assisted dispersion shows better distribution of clays particle in NBR matrix in spite of showing tendency to agglomerate due to increased filler loading. One can see clearly the agglomerated clays particles in case of conventional mixing Fig.5.9 (b & c). Fig.5.9 (c) shows better distribution than that of Fig.5.9 (b) as that also can be attributed to increased amount of nanofillers leads to agglomeration and plateau formation on the surface of the nanocomposite due to lack of dispersion without DOP assisted dispersion. Hence, it can extracted from the SEM analysis that DOP assisted dispersion was fairly better than conventional mixing leading to improvement in various other properties.

5.8 Conclusion

1. Dioctyl Phthalate was used to disperse the nanoclay in NBR rubber matrix and the dispersion of nano particles were found better.

2. The dispersion of nanoclay was studied using Scanning Electron Microscopy and found to be uniform through out the polymer matrix. The presence nanoclay in NBR matrix increases the thermal resistance of the polymer composites.

3. The improvement in the mechanical properties indicates that nanoclay reinforces the polymer matrix.
5.9 References

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15. K. A. Dubey, Y.K Bharwaj, C.V Chaudhari, N. K Goel, S. Sabharwal, 


20. Enhanced interfacial interaction of rubber/clay nanocomposites by a novel two-step method Qing-XiuJia a, You-Ping Wu b, Yi-Qing Wang a, Ming Lu b, Li-Qun Zhang a,b,*
