Chapter VIII

Results and Discussion – HNBR Polymer Nanocomposites using DOP as dispersion aid
CHAPTER VIII : HYDROGENATED NITRILE BUTADIENE RUBBER (HNBR) NANOCOMPOSITES WITH DOP AS DISPERSION AID

Introduction

Hydrogenated nitrile rubber (HNBR) has become a fast growing raw material used in the production of rubber articles for the automotive industry as well as for other specialized industrial applications such as oil drilling and roll covers. Its success can be attributed to its unique combination of properties. More and more often HNBR is selected to replace other polymers because of its good balance of low temperature flexibility, high static and dynamic mechanical strength, abrasion resistance, and good heat and chemical resistance. At the same time however, there is increasing demand from the end users to extend the service life of the rubber articles, even while the service environments become progressively more aggressive to rubber articles. With rising under the hood temperatures in new cars, the aging resistance of a polymer during the lifetime of an automobile has become a focal point for research and development efforts in the rubber industry. Hydrogenated nitrile rubber (HNBR) has been developed to improve thermal stability of nitrile butadiene rubber (NBR) [1-3]

8.1 Rheological Properties

Rheological data of compounds were tabulated in Table 8.1 and Table 8.2. Nanoclay dosage doesn’t affect much the curing time of the compound, since optimum cure time of the HNBR nano compounds remains almost same. The torque values were increasing with the addition of nanoclay dosage. From the study of the effect of nanoclay content on rheometric torque of HNBR nanocomposites, it was observed that the minimum torque, an indirect measure of viscosity of the compound, marginally increased gradually as nanoclay content increases in both the cases of 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.
Table 8.1 Rheological properties of HNBR-Nanoclay compounds prepared by conventional mixing

<table>
<thead>
<tr>
<th>Rheological Properties</th>
<th>HNC0</th>
<th>HNC1</th>
<th>HNC3</th>
<th>HNC5</th>
<th>HNC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum torque (lbs. inch)</td>
<td>46.71</td>
<td>48.11</td>
<td>50.22</td>
<td>50.54</td>
<td>53.36</td>
</tr>
<tr>
<td>Minimum torque (lbs. inch)</td>
<td>4.27</td>
<td>4.45</td>
<td>5.32</td>
<td>5.62</td>
<td>5.75</td>
</tr>
<tr>
<td>Optimum cure time (t_{90}, (min)</td>
<td>20.11</td>
<td>19.30</td>
<td>19.47</td>
<td>19.66</td>
<td>19.08</td>
</tr>
</tbody>
</table>

Table 8.2 Rheological properties of HNBR DOP assisted dispersion mixing of Nanoclay in HNBR

<table>
<thead>
<tr>
<th>Rheological Properties</th>
<th>HNDC1</th>
<th>HNDC3</th>
<th>HNDC5</th>
<th>HNDC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum torque (lbs. inch)</td>
<td>48.603</td>
<td>50.31</td>
<td>51.61</td>
<td>52.07</td>
</tr>
<tr>
<td>Minimum torque (lbs. inch)</td>
<td>4.42</td>
<td>5.14</td>
<td>5.23</td>
<td>5.84</td>
</tr>
<tr>
<td>Optimum cure time t_{90}, (min)</td>
<td>20.03</td>
<td>19.29</td>
<td>19.67</td>
<td>19.38</td>
</tr>
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</table>

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 HNBR chains into the galleries of the nanoclay resulting in better interaction between the nanoclay and the rubber matrix\textsuperscript{[17]}. But here, it is clearly noticeable that there is similar characteristic exhibiting in case of DOP assisted dispersion of nano-clays with a small differences between HNC7 and HNDC7.

8.2 Mechanical Properties

As the loading of nano filler increases due to the reinforcement of polymer – filler interaction all the mechanical properties were increased.
8.2.1 Tensile strength

Tensile strength was increased with the dosage of Nanoclay in HNBR compounds as shown in Fig. 8.1 for composites prepared by dispersed mixing of nanoclay in DOP oil shown good improvement in Tensile strength compared to normal mixed compounds. Among pre-dispersed samples more improvement in properties were observed for 3 phr composites. This was mainly due to the good quality of dispersion. As the Nanoclay varies from 3 to 7, the viscosity increased and a stage reached in which further addition will not differentiate the normal mixed and dispersed compounds. So the difference in properties of HNC & HDNC compounds decreased with the increase in phr.

![Fig. 8.1 Effect of nanoclay dispersions on TS of HNBR - Nanocomposites](image)

8.2.2 Tensile modulus

All tensile modulus properties were increased with increase in Nanoclay dosage due to the efficient reinforcement of nanoparticles as shown in Table 8.3 at 100 % modulus well pre-dispersed nano clay compounds had better properties than normally mixed compounds as expected. But after this HNC compounds shown better modulus than HNDC compounds.
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Table: 8.3 Tensile modulus of PNCs with different loading of nano clay in HNBR matrix

<table>
<thead>
<tr>
<th>Modulus</th>
<th>HNC0</th>
<th>HNC3</th>
<th>HNC5</th>
<th>HNC7</th>
<th>HNDC3</th>
<th>HNDC5</th>
<th>HNDC7</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>

This is due to reduced stress withstanding nature of properly mixed clay compounds after 100 % elongation which again proved the slipping mechanism of dispersed nano clay layers without reducing the tensile strength. For normal mixed samples, after 100 % elongation, the non-dispersed stacks of Nanoclay layers separates and this needs more force for layer separation compared to uniformly pre-dispersed HNBR nano compounds.

8.2.3 Elongation @ break

The elongation @ break of Nanoclay compounds increased with dosage Fig.8.2 and elongation properties of dispersed compounds were better compared to normal mixed compounds due to the facts that the nanofillers may increase the tear energy and hence it holds to elongates more longer length than that of the sample which do not contains nanofiller.

![Fig. 8.2 Effect of nanoclay dispersions on EB % of HNBR – Nanocomposites](image-url)
8.2.4 Hardness

Resistance to indentation was increased significantly as it is clear from the Fig 8.3. The resistance to indentation of PNCs were increasing with an increase of nano filler loading.

![Graph showing hardness vs dosage of nanoclay](image)

**Fig.8.3** Effect of nanoclay dispersions on Hardness of HNBR - Nanocomposites

This increase in hardness can be attributed to the facts that the doses of nanoclays develops the compactness in composite at the very fine level might be filling the gap between molecular chains and also resisting the chain movement which leads to resistance to indentation.

Further more the hardness was found to be the same for both the types of series sample respective level of loading. This shows that the hardness will not be changed even with the better dispersion but there is significant improvement in other mechanical properties.

8.3 Tear strength

Tear strength of nanoclay compounds increases with increase in dosage of nanoclay Fig.8.4. This is mainly due to the efficient filler – filler networks formation. Compared to HNDC compounds HNC compounds have good tear strength. This is due to the non dispersed stacks of clay layers present in the normally mixed nano compounds restrict the crack propagation compared to properly dispersed one. In HNDC compounds the uniformly dispersed nano clay layers are unable to resist the crack growth.
8.4 Compression set

Compression set was carried out in 200 °C for 24 hrs as per ASTMd - 395 method. Compressions set properties of HNBR nano composites were improved with the addition of nanoclay (Fig. 8.5). The 7 phr Nanoclay composites resist the compressive strain more even at 200 °C in which the loss of plasticizer itself can cause properties loss, but due to the properly dispersed Nanoclay networks, the properties were enhanced and which is responsible for entire set properties even it contains 20 phr oil.
16% improvement in properties was observed while varying the nano-composites from 3 to 7 phr mixed in normal way. For pre-dispersed samples, this improvement is again raised to 20%. This is due to the ability of dispersed nanoclay layers for withstanding the force developed due to compressive strain.

8.5 Air Permeability studies

Barrier properties i.e., air permeability of Nanoclay containing compounds reduced with the addition of nanoclay in HNBR as in Fig.8.6. This improvement was more observed in pre-dispersed compounds. For normal mixed compounds with the addition of 7 phr nanoclay permeability reduced by 20%. In the case of predispersed composites same impermeability was attained in 3 phr dosage. And for 7 phr pre-dispersed samples it has improved to 60%. This improvement was observed in permeability due to the intercalated layered structure of nanoclay. While increase the dosage the interlayer spacing reduced and so permeability increased.

Fig. 8.6 Effect of nanoclay dispersions on air permeability of HNBR - Nanocomposites
8.6 TGA Studies

The thermograms of PNCs with dispersed mixed nanoclay is given Fig.8.7 shows that there is an increase in initial and maximum degradation temperature of PNCs. For cross linking type of polymers, the thermal stability is expected to improve due to the formation of more compact three dimensional cross-linking networks, which is more thermally stable. And as a result, the degradation temperature of nano-composite shifted from 487 °C to 497 °C with increase in dosage of nanoclay. That means the thermal stability was improved by 10 °C with the addition of 7 phr of nanoclay in HNBR matrix.

![TGA Thermograms](image)

**Fig. 8.7** Effect of nanoclay dispersions on Thermal stability of HNBR - Nanocomposites

8.7 Scanning Electron Microscopy –

Fig. 8.8 [a to c] shows scanning electron micrographs of tensile fracture surface of HNBR based polymer Nano-composites (HNC). It is clearly observed from the figure (a) to (c) that it is very difficult to disperse clay nanoparticles uniformly in to HNBR matrix by conventional mixing process due to its agglomerative nature and high surface area and energy.
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Fig. 8.8 Scanning Electron Micrographs of HNBR Nanoclay composites

The SEM micrographs from Fig (d) to (f) show better distribution of particles of nanoclay fillers in the matrix, of course this process also have not achieved desired level of dispersion but study suggests that DOP assisted dispersion of has improved the distribution of nano-clays in to the polymer matrix.

8.7 Conclusion

1. Di-octyl Phthalate was used to disperse the nanoclay in HNBR rubber matrix and the dispersion of nano particles were found good.
2. The dispersion of nanoclay was studied using Scanning Electron Microscopy and found to be uniform throughout the polymer matrix.
3. The presence of nanoclay in HNBR matrix increases the thermal resistance of the polymer composites.
4. The improvement in the mechanical properties indicates that nanoclay reinforces the polymer matrix. Permeability / Barrier properties improved significantly.
8.10 References

5. E.P. Giannelis, Adv Mater; 8, 29, 1996,
17. Effect of DOP as dispersion medium on MMT nano clay in NBR polymer matrix, ISSN-2249-555X Volume 4, Issue 2, February 2014)

Papers published in peer reviewed journals from Ph.D. work:


Papers presented in National & International Conferences

Technical papers out of this research work have been presented in the following national and international conferences:

<table>
<thead>
<tr>
<th>S.No</th>
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<tr>
<td></td>
<td>International Conference entitled “Nano Technology Materials and Composites for Frontier Applications”</td>
<td>October, 2010</td>
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<td></td>
<td>on “Advances in Polymer Science and Rubber Technology”</td>
<td>2011</td>
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<td>3.</td>
<td>IRMRA’s 21st Rubber conference, National Conference</td>
<td>20-21st Jan 2012</td>
<td>Processing of nano fillers in Nitrile Rubber- a Novel technique</td>
<td>Organized by IRMRA, Thane</td>
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<td>8.</td>
<td>International Research Fair, Global Rubber, Latex &amp; Tyre Expo, Bangkok</td>
<td>11-15th Mar 2014</td>
<td>“Improvement of thermal resistance of polymers by using Nano fillers”</td>
<td>Technobiz Bangkok, Thailand</td>
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