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# Effect of DOP as Dispersion Medium on MMT- nano Clay in NBR Polymer Matrix

KEYWORDS: Nano-clay, NBR, DOP, Morphology, Mechanical properties, Permeability


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**ABSTRACT** *Dispersed polymer/clay nanocomposites are of great interest because they significantly improve the properties of polymeric materials. However, achieving a good dispersion of nanoclay has been a big challenge. An attempt was made to disperse nanofillers in NBR matrix using DOP]. The mixing was carried out using two roll mill and Rheological properties were studied using Rubber Process Analyzer [RPA]. Physical properties were studied using Zwick-UTM. Barrier properties found significantly improved when DOP used as dispersion media.*

## Introduction

In the recent years, polymer nano-clay composites found to have greater 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 properties that are synergistic combinations of the individual components with the reinforcing components are 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 nm) within the polymer matrix. Elastomers were reinforced with fillers to improve their performance by incorporating conventional fillers. 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. NBR-Nano graphite polymer nano composites were found to increase its thermal stability [13]. Dispersion of nanosilica in NBR polymer was studied by Rajkumar at.al.[14]

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.-1). The intercalated structure results from penetration of a few polymer chains into the silicate interlayer. The best property improvements in polymer composites and the least influence to viscosity for low molecular weight suspensions results from the exfoliated morphologies.

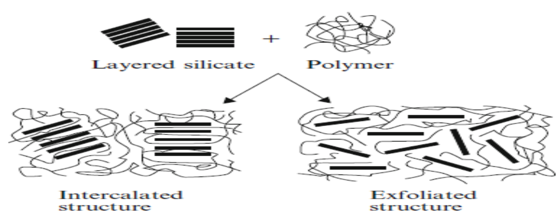


**Figure-1**

Di-octyl-Phthalate is still used on a widely spread base all around the world. Almost every product made of soft plastic needs Di-octyl-Phthalate in order to make the material more flexible and smooth. Therefore, DOP has been a most important ingredient in polar rubber processing. To overcome the dispersion problem, we adopted a new technique to incorporate nano-clay in Acrylonitrile Butadiene Rubber (NBR) matrix using Di-octyl 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 improvement using DOP in the changes in morphology, permeability and mechanical properties were studied.

### 2. Materials:

Acrylonitrile Butadiene Rubber, MMT organo modified Nano Clay, Sulphur, TDQ, stearic acid Zinc oxide, 6PPD and Di Octyl Pthalate oil were obtained from reputed suppliers.

### 2.1. Compounding

**Table 1. Compound Formulations**

| Compounding Ingredients | NBC0 | NBC1 | NBC3 | NBC5 | NBC7 |
|---|---|---|---|---|---|
| NBR-JSR 230 | 100 | 100 | 100 | 100 | 100 |
| Sulphur | 2 | 2 | 2 | 2 | 2 |
| Zinc oxide | 4 | 4 | 4 | 4 | 4 |

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|---|---|---|---|---|---|
| Stearic acid | 1 | 1 | 1 | 1 | 1 |
| Nano Clay | 0 | 1 | 3 | 5 | 7 |
| DOP | 10 | 10 | 10 | 10 | 10 |
| TDQ | 1 | 1 | 1 | 1 | 1 |
| 6PPD | 1 | 1 | 1 | 1 | 1 |
| MBTS | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |

**2.1.1 Conventional Mixing:**
Polymer nano compounds were prepared by mixing NBR and other compounding chemicals as per formulation given in table 1 using a open two roll mixing mill as per ASTM method.

**2.1.2 Mixing with dispersed nanoclay**
In NBDC mixes, Nano clay is dispersed in DOP oil and sonicated to disperse the Nanoclay in DOP. Pre-dispersed nanoclay was added to NBR and other compounding chemicals as per table 1, using an open two roll mixing mill and the speed ratio of the two rolls were maintained at 1:1.2.

**2.1.3. Preparations of Specimens**
Polymer nano compounds were kept 16 hrs for maturation. Then the compounds were moulded using compression moulding press to obtain vulcanizate of sheets and buttons as per ASTM standard.

**3. Testing and Characterization**
**3.1 Rheological studies & Strain sweep analysis**
Rheological properties like optimum cure time and maximum torque determined using Monsanto Rheometer at 160˚C for 30 mints and sweep studies of cured compounds were carried out using Rubber Process analyzer [RPA-2000, Alpha Tech-USA]. The compound was cured as per optimum cure time obtained from Monsanto Rheometer at 160 ˚C for 20 mints.

**3.2 Mechanical Properties**
Mechanical properties and Tear strength were measured using Testing Machine [UTM-Zwick] according to ASTM D 412 and ASTM 624 respectively with cross head speed of 500 mm/min at RT. Shore Hardness was measured with a Durometer as per ASTM D 2240.

**3.3 Permeability studies**
Air Permeability were carried out as per IS 3400 (Part 21) and an absolute pressure in 4 bar was kept constant and assembled test samples are mechanically conditioned initially for 24 hrs, and permeability was measured at RT

**3.4 SEM – EDS analysis**
Morphological studies of polymer nanocomposites were carried out using Scanning electron microscope [SEM, Zeiss].

**4. Results and Discussion**
**4.1 Rheological Properties**
Rheological data of compounds were tabulated in table 2. Nanoclay dosage doesn't affect much the curing time of the compound. The MMT clay may form complex with sulphur and facilitate increase in cure rate. [15].

**Table: 2 Rheological data of NBR- Nanoclay composites**

| Curing properties | NBC0 | NBC3 | NBC5 | NBC7 | NBDC3 | NBDC5 | NBDC7 |
|---|---|---|---|---|---|---|---|
| Maximum torque, Lbs | 38.76 | 36.94 | 33.23 | 30.86 | 34.65 | 34.18 | 31.40 |
| Minimum torque, Lbs | 6.21 | 6.86 | 6.89 | 6.93 | 6.32 | 6.69 | 7.28 |
| Optimum cure time T 90, minutes | 4.08 | 3.99 | 4.06 | 4.09 | 4.33 | 4.12 | 4.11 |

Table-2 indicates that nanoclay content in polymer matrix increases the minimum torque which is an indirect measure of viscosity of the compound. The maximum torque depends on both the extent of cross-linking 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 intercalation of NBR chains into the galleries of the nanoclay. There has been difference in DOP assisted mixed compounds which could be due to better dispersion and de-agglomeration of the nanofiller particles in the matrix.

**4.2 Mechanical Properties**

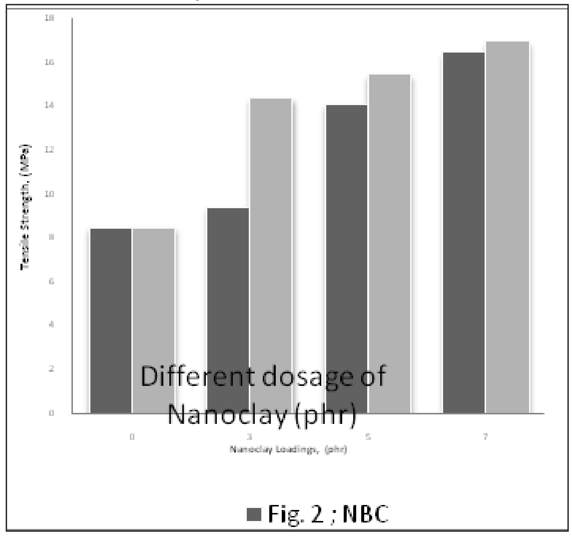


Fig. 2 shows that Tensile strength increases with increase in dose of nanofillers and after attaining optimum, it decreases. The pre-dispersed nanofiller system shows further improvement in tensile properties even with lower dose of nanofiller. A significant increase in tensile strength found with pre-dispersed nanoclay with 3 phr as depicted in Fig-2.

The elongation @ break of pre–dispersed Nanoclay compounds gradually decreases with dosage (fig.3) due to improvement in reinforcement.

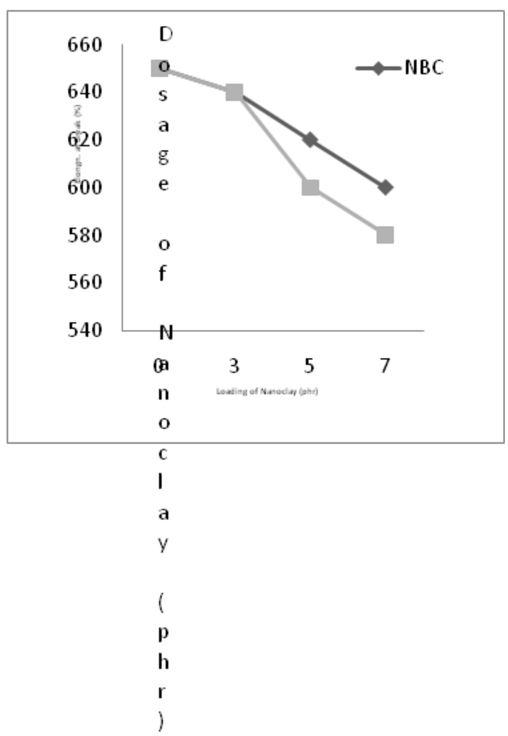


**Fig.3. Elongation @ break of NBR nanocomposites**

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Hardness is defined as the resistance to indentation. Fig.4 depicts the increase in hardness due to filler loading which is due to increase in stiffness of rubber nanocomposites.

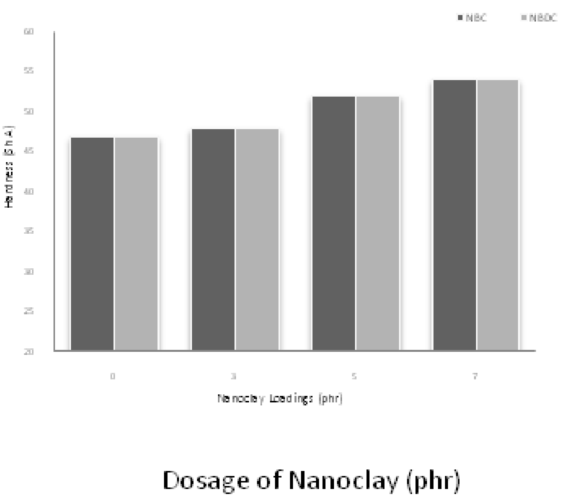



**Fig.4. Shore A Hardness of NBR based nanocomposites**

The hardness of nanocomposites found almost similar for the pre-dispersed nanoclay system and hence, dispersion does not affect the hardness of system

### 4.3 Tear strength

Tear strength of Nanoclay composites increases with increase in dosage of Nanoclay. (fig.5).

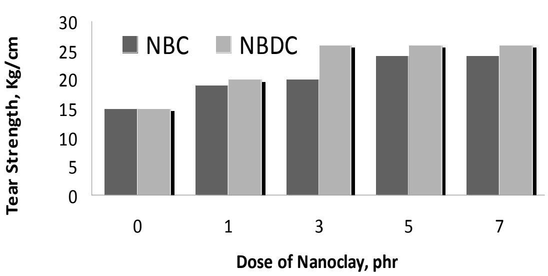



**Fig.5. Tear strength of NBR nanocomposites**

Due to increase in reinforcement, nanofilled composites found to have more tear strength at 3phr we can see a 30 % improvement in tear strength for pre-dispersed composites compared to the conventional one. Hence, the dispersion helps in enhancement of failure properties.

### 4.4 Air Permeability studies

The transport behaviour through composites depends on the type of filler, matrix, temperature, size of 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 Nanocomposites decreases with the addition of nanoclay in NBR up to 5 phr significantly and then decreased abruptly. And the improvement up to 5phr 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 impermeabilty was more observed in pre-dispersed compounds due to its better dispersion.

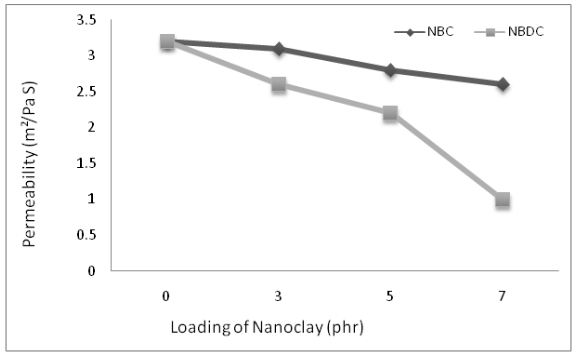
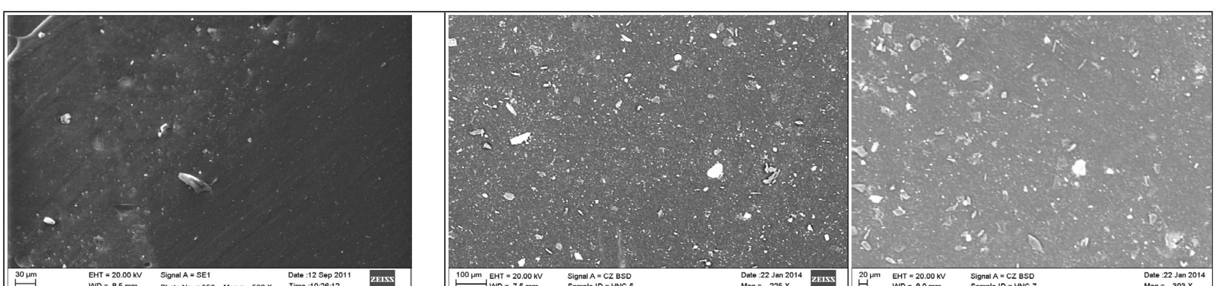



**Fig.6. Permeability of NBR nanocomposites in different loadings of nanoclay**

The decreased permeability of clay nano composite arises from the longer diffusion path that the gas must penetrate 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 [16] and Bharadwaj [17] 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.

### 4.5 Scanning Electron Microscopy

**Fig-7 [a to c]** shows scanning electron micrographs of tensile fractured surface of NBR Nano-composites. The **Fig.7(a)** shows the mapping of the NBR composite without clay i.e virgin, **Fig-7(b) Fig. (c)** show the dispersion of 5 phr of nanoclay in NBR matrix with conventional method mixing and pre-dispersed DOP nanoclay. The pre-dispersed nanoclay showed better dispersion in the matrix than the conventional one.



| 7 (a) NBC0 | 7 (b) NBC 5 | 7 (c) NBDC 5 |
|---|---|---|

**Fig. 7 Scanning Electron Micrographs of NBR Nanoclay composites**

### 5.0 Conclusion

Di-octyl Phthalate was used to disperse the nano-clay in NBR rubber matrix and the dispersion of nano particles were found good. The presence of nano-clay in NBR matrix show improved performance on barrier properties and mechanical properties of nanocomposites with increasing loading of clay nanofiller.

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