Preparation, characterization and properties of polymeric nanocomposites based on natural rubber and polybutadiene rubber blend

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Abstract: Nanocomposites based on natural rubber and polybutadiene rubber blend were prepared by employing different amounts of modified layered silicate. X-ray diffraction was used to determine the structure of prepared nanocomposites. The effects of incorporation of organically modified clays on vulcanization reactions of the rubber blend were analyzed by using oscillating disk rheometer. High reduction in scorch time and optimum cure time was observed when organoclay was added and this was attributed to the amine groups of the organic modifier. Tensile strength, modulus, abrasion resistance and tear strength improved significantly on adding organoclay and there was a good correlation between abrasion resistance and tear strength of the nanocomposites. Elongation at break decreased by using organoclay and increase in loading of organoclay up to 10 phr and further led to decrease in the rate of variation of tensile properties. Thermal stability of the blend was improved by using 5 phr organoclay.

Introduction

Reinforcement is very important for rubber products and carbon black was the first and most important reinforcing filler used in elastomeric compounds. But polluting nature, monotonous black colour and dependence of carbon black on petroleum caused researchers to use other reinforcing materials [1]. Clay has been used as rubber filler for many years. The reinforcing ability of clay is poor because of its big particle size. Clay is composed of many mono-layers that are 1 nm in thickness and the lateral dimensions of these layers may vary from 300 Å to several microns and even larger, depending on the particular silicate [2]. With respect to this subject, a new way was recently found to improve the reinforcing ability of clay through using some special processing methods. Using these methods polymer/clay nanocomposites have been developed which attracted considerable attention for both scientific challenges and industrial applications since they impart a remarkable improvement on material properties. The high reinforcing effect of layered silicate, even at low loading, is largely due to the nanoscale dispersion and the very high aspect ratio of silicate platelets [1-4].

The clays are hydrophilic and less compatible with organic polymers. Then for majority of polymers, owing to their hydrophobic character, the clay must be modified to enhance its compatibility with polymers. The clays can be modified with various alkylammonium salts. Modification expands interlayer distance of the layered silicate,
reduces the surface energy [5, 6] and enhances penetration of polymers into the galleries.

Polymer/clay nanocomposites have been prepared by various methods including in situ polymerization [7, 8] melt intercalation [9, 10], latex blending [11, 12] and solution blending [13, 14].

The intercalation/exfoliation of layered silicates are governed by the compatibility, polymer diffusivity and processing variables. Among the processing variables, attention should be paid to the locally acting shear forces [15]. Rubbers exhibit very high viscosities due to their high molecular weight and generate high shear forces locally during melt mixing with organoclay which lead to break up of the layered structure of silicates and delaminating of the silicate layers [16]. Thus melt intercalation is an appropriate method to produce elastomeric based nanocomposites. To prepare elastomeric nanocomposites, variety of studies have been conducted on different kinds of elastomers such as natural rubber (NR), butadiene rubber (BR), styrene butadiene rubber (SBR), ethylene-propylene-diene monomer (EPDM) and nitrile-butadiene rubber (NBR). A deeper understanding of the influence of nanoparticles on the rubber curing is of crucial importance to explain the improved properties of these nanocomposites [17].

Blending of elastomers is an effective method for altering the performance of elastomers. Blends of natural rubber and polybutadiene rubber are commonly used at tire industries. To the best of our knowledge, the effect of organoclay on blend of natural rubber and butadiene rubber (NR/BR blend) has not been studied and reported by other researchers yet [18]. In this study attempts have been made to prepare nanocomposite based on NR/BR/organoclay through melt intercalation method. Prepared nanocomposites contained different amount of organoclay. Structure of the nanocomposites and its effect on properties and curing behaviour of the compounds were investigated and reported.

**Results and discussion**

**Curing characteristics**

Figure 1 shows vulcanization curves for NR/BR blend and NR/BR/organoclay nanocomposites. Curing characteristics of all prepared compounds have been reported in Table 1. As it can be seen the vulcanization rate was increased. Scorch time ($t_s$) and optimum cure time ($t_90$) of the compound were greatly decreased when 5 phr organoclay was added to the NR/BR blend. These results indicate that the organoclay has accelerated vulcanization reaction in NR/BR compound. This effect of organoclay on vulcanization of polybutadiene rubber [19-21] and natural rubber [22, 23] has also been reported which was attributed to the ammonium groups in the nanosilicate structure which come from the modification process of clay. A transition complex formation with amines and sulphur facilitates the development of elemental sulphur [21, 24] and affects the curing reaction of rubber. The scorch and optimum cure times of the nanocomposites gradually decreased with further addition of organoclay (Table 1). Similar trends in the vulcanization characteristics of NR/organoclay nanocomposites have been reported by other researchers [25].

The difference between maximum and minimum torque of rheometry ($MH – ML$) was increased by the addition of 5 phr organoclay into the compounds which can be attributed to increase in crosslink density of the vulcanized samples. However, further
loading of organoclay resulted slightly decrease in \((\text{MH} - \text{ML})\). The results showed that using of organoclay in NR/BR blend leads to much higher variation of compound curing characteristics compared to using it in a NR based compound [26].

**Fig. 1.** Effects of organoclay content on curing behaviour of NR/BR blend.

**Tab. 1.** Curing characteristics of the prepared compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(t_2) (s)</th>
<th>(t_{90}) (s)</th>
<th>(\text{MH} - \text{ML}) (dN.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/BR</td>
<td></td>
<td></td>
<td>20.2</td>
</tr>
<tr>
<td>NR/BR/5 phr organoclay</td>
<td>81</td>
<td>198</td>
<td>27.7</td>
</tr>
<tr>
<td>NR/BR/10 phr organoclay</td>
<td>72</td>
<td>195</td>
<td>27</td>
</tr>
<tr>
<td>NR/BR/15 phr organoclay</td>
<td>67</td>
<td>193</td>
<td>24.4</td>
</tr>
</tbody>
</table>

**Structure of nanocomposites**

Figure 2 shows the XRD diffraction patterns of organoclay and NR/BR/organoclay nanocomposites which contain different amount of organoclay. As it can be seen in this figure the organoclay and prepared nanocomposites show three peaks denoted as 001, 002 and 003. The lowest diffraction peaks of the patterns represent the 001 plane reflections of the silicate layer. The organoclay displays a broad intense peak at around \(2\theta = 2.81^\circ\), corresponding to a basal spacing of 3.14 nm. This peak for the nanocomposites containing 5, 10 and 15 phr organoclay can be observed at 2.23°, 2.21° and 2.25° which correspond to interlayer spacing of 3.96, 3.99 and 3.92 nm, respectively. In fact, intergallery distances in all of prepared nanocomposites are larger than the initial value of the used organoclay indicating that the rubber molecules have been intercalated into the organoclay interlayer. Also 002 and 003 diffraction peaks are slightly shifted to lower angles in the XRD patterns of the NR/BR/organoclay nanocomposites. The obtained XRD data for the NR/BR/organoclay
nanocomposites is summarized in Table 2. High-acting shear stress on the layers and presence of polar curing agents favour the intercalation of the rubber chains into the galleries and the dispersion of the layered silicates in the matrix. Due to extremely high viscosities of rubbers during melt mixing, high shear stress acts on the clay layers and results in the peeling off of the layers [16]. Also, curatives such as ZnO, MBTS, stearic acid, and sulphur, which are polar low-molecular weight materials may penetrate between organoclay layers and result in crosslinking of rubber inside the galleries of the layered silicate [21].

![Graph showing X-Ray diffraction patterns of organoclay and NR/BR/organoclay nanocomposites.](image)

**Fig. 2.** X-Ray diffraction patterns of organoclay and NR/BR/organoclay nanocomposites.

**Tab. 2.** X-Ray diffraction data of NR/BR/organoclay nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>001 (nm)</th>
<th>002 (nm)</th>
<th>003 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>organoclay</td>
<td>3.14</td>
<td>1.92</td>
<td>1.25</td>
</tr>
<tr>
<td>NR/BR/5 phr organoclay</td>
<td>3.96</td>
<td>1.98</td>
<td>1.34</td>
</tr>
<tr>
<td>NR/BR/10 phr organoclay</td>
<td>3.99</td>
<td>1.97</td>
<td>1.36</td>
</tr>
<tr>
<td>NR/BR/15 phr organoclay</td>
<td>3.92</td>
<td>1.96</td>
<td>1.33</td>
</tr>
</tbody>
</table>

*Properties of the vulcanized nanocomposites*

-Tensile Strength

Table 3 illustrates the effects of the organoclay loading on the final properties of the NR/BR/organoclay nanocomposites. The results (see Figure 3) show the tensile strength of the nanocomposites increases significantly by adding 5 phr organoclay and then gradually increases with further adding organoclay in the compound. This reinforcing effect of organoclay is believed to be related to the nanoscale dispersion...
of organoclay in the matrix and intercalation/exfoliation process [24]. Also, it can be attributed to high aspect ratio and platelet structure of organoclay [27, 28].

**Tab. 3.** Properties of the prepared NR/BR/organoclay nanocomposites.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sample</th>
<th>NR/ BR Gum</th>
<th>NR/ BR/ 5 phr organoclay</th>
<th>NR/ BR/ 10 phr organoclay</th>
<th>NR/ BR/ 15 phr organoclay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td></td>
<td>3.7</td>
<td>11.9</td>
<td>13.9</td>
<td>15.4</td>
</tr>
<tr>
<td>Stress at 300% (MPa)</td>
<td></td>
<td>1.26</td>
<td>2.82</td>
<td>3.91</td>
<td>4.69</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td></td>
<td>643</td>
<td>600</td>
<td>577</td>
<td>565</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td></td>
<td>44</td>
<td>53</td>
<td>58</td>
<td>63</td>
</tr>
</tbody>
</table>

**Fig. 3.** Effects of organoclay content on tensile properties of the nanocomposites.

-Tensile Strain
As shown in Figure 3, the elongation at break of the nanocomposite decreased significantly with incorporation of 5 phr organoclay and it decreased moderately with further loading of organoclay. In fact, intercalation/exfoliation of the organoclay reduces the mobility of the rubber molecules and therefore the elongation at break decreases. This decreasing of elongation at break also can be due to increasing of agglomeration tendency of organoclay at higher loading [25].
-Hardness and 300% Tensile Stress

The stress at different elongations (100% and 300%) follows the same trends as the tensile strength of the nanocomposites (Table 3). The hardness of nanocomposites also increases by increasing the amount of organoclay. It is attributed to the layer structure of the clay and the extremely high interfacial action between the layer or layer bundle and the rubber.

-Abrasion loss and tear strength

Figure 4 shows the trend of abrasion resistance and tear strength with increasing amount of organoclay in the compounds. As the figure shows the abrasion resistance as well as the tear strength of the nanocomposites increased with increase of organoclay loading. This figure also shows a good correlation between abrasion resistance and trouser tear strength of nanocomposites, in fact abrasion resistance can be predicted by measuring tear strength.

Fig. 4. Effect of organoclay content on abrasion resistance and tear strength of the nanocomposites.

-Thermal stability

Figure 5 shows the thermogravimetric curves for the NR/BR blend and its nanocomposites with various amount of organoclay. As it can be seen in this Figure, the start degradation temperature of NR/BR blend slightly increases by incorporation of 5 phr organoclay, however the rate of degradation significantly decreases. The enhancement in thermal stability of nanocomposites is attributed to the penetration of the polymer chains into the galleries of the organoclay. The clay nanolayers prevent out-diffusion of the volatile decomposed products [29]. This effect may also be attributed to the increase in the crosslinking density. In general, thermal stability of a vulcanizate increases with increasing crosslinking density [30]. Comparison of thermogravimetric curves for the nanocomposites contain different amounts of
organoclay indicates that thermal degradation of NR/BR/organoclay does not significantly vary with further (10 and 15 phr) loading of organoclay (Figure 5).

![Thermogravimetric analysis of prepared compounds with and without organoclay.](image)

**Fig. 5.** Thermogravimetric analysis of prepared compounds with and without organoclay.

**Conclusions**

The obtained results in this work showed that organoclay effectively accelerate the vulcanization reaction of NR/BR blend, and this can be attributed to the intercalated materials used to modify the clay. When the organoclay loading increased, the scorch time and optimum cure time slightly decreased. The rate of curing and difference between maximum and minimum torque of rheometry (MH-ML) increased significantly by adding 5 phr organoclay and (MH-ML) slightly decreased with further incorporation of organoclay. The XRD results indicated that NR and BR molecules have intercalated the interlayers of organoclay which resulted in the increase of interlayer distance. Tensile strength, modulus, hardness, abrasion resistance and tear strength increased with the increase of organoclay content while the elongation at break decreased moderately. The obtained results exhibited that using of organoclay in NR/BR blend leads to much higher variation of compound curing characteristics and tensile properties compared to using it in a NR based compound. A good correlation between abrasion resistance and trouser tear strength of nanocomposite was observed. The rate of thermal degradation of nanocomposites greatly decreased with incorporation of 5 phr organoclay and further loading of organoclay did not significantly affect this property.

**Experimental**

**Materials**

NR (SMR GP grade) with a Mooney viscosity of ML (1+4) 100 °C = 61 was obtained from Malaysia and BR (BR1220) with ML (1 + 4)100 °C=45 supplied by Arak
Petrochemical Co, Ltd (Arak, Iran). Organically modified montmorillonite (organoclay) was purchased from Southern Clay Products (Gonzales, TX) under the trade name of Cloisite 15A. This organoclay was modified by dimethyl dihydrogenated tallow quaternary ammonium with a concentration of 125 mequiv/100 g of clay. Sulfur was supplied by Tesodak, ZnO by Sanaye Rangineh Pars, stearic acid by Unichema, MBTS and PAN by Bayer Company.

**Preparation of the nanocomposites**

Composition of the prepared nanocomposites is listed in Table 4. To mix ingredients of the nanocomposites, a Brabender internal mixer (PL 2200, Germany) was employed at 80 °C. Mixing was carried out at rotor speed of 90 rpm for 15 min. At first NR, BR, organoclay, zinc oxide, antioxidant, and stearic acid were mixed in the internal mixer. Then sulphur and accelerator, MBTS, were added to the compounds on a two-roll mill.

**Tab. 4.** Composition of the prepared nanocomposites.

<table>
<thead>
<tr>
<th>Material</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>60</td>
</tr>
<tr>
<td>Butadiene rubber</td>
<td>40</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.5</td>
</tr>
<tr>
<td>MBTS¹</td>
<td>1</td>
</tr>
<tr>
<td>PAN²</td>
<td>1</td>
</tr>
<tr>
<td>Cloisite 15A organoclay</td>
<td>various (0, 5, 10, 15)</td>
</tr>
</tbody>
</table>

¹Benzothiazyl disulfide.  
²Phenyl Alfa-Naphthylamine.

To prepare specimens for measuring physical and mechanical properties of the vulcanizates, compounds were cured into 2 mm thick sheets in a standard mould at 160 °C under pressure of 8 MPa in an electrically heated hydraulic press to their respective cure times \( t_{90} \), which were determined by using an oscillating disk rheometer.

**Characterization**

**Wide-angle X-ray diffraction**

A Philips (Munich, Germany) model of wide-angle XRD equipment with Ni-filtered CuKα radiation was used to study the expansion of the clay interlayer distance. The d-spacing of the silicate layer was calculated with Bragg’s equation:

\[
nλ = 2d \sin \theta
\]

where \( \lambda \) is the wavelength of the X-ray \( \lambda = 0.1542 \text{ nm} \), \( d \) is the basal spacing of the silicate layer, and \( \theta \) is the angle of incident radiation. The samples were scanned in the 2θ range from 1 to 10° at a rate of 1.2 °/min.
Curing characteristics
Curing characteristics of nanocomposites were measured according to ASTM D2084 by using ODR 100S Monsanto rheometer apparatus at ±3º oscillation angle. Scorch time \((t_2)\), optimum cure time \((t_{90})\), and also the difference between minimum and maximum torque of rheometry were determined.

Properties of the vulcanized nanocomposites
Tensile properties were measured on dumbbell shaped specimens punched out from the moulded sheets using ASTM Die - C by Galdabini Sun 2500 universal testing machine in accordance with ASTM D412, a standard test method for measuring tensile properties of vulcanized rubber. Tests were carried out at room temperature and cross-head speed of 500 mm.min\(^{-1}\).

A Zwick hardness tester was employed according to ASTM D2240 for measuring hardness of the prepared samples.

Abrasion tests were performed according to ASTM D2228 on a Zwick abrasion tester. The abrasion was defined as inverse of the mass loss of a sample.

Trouser tear test method, ASTM D624, was employed to determine tear strength of the nanocomposites. To measure each property, three specimens were tested and average values determined and reported.

Thermal stability
Thermal Gravimetric Analysis provides information on thermal degradation of polymer. A Thermo Gravimetry analyzer (TGA Instrument, DuPont 951) was used to assess the influence of organoclay on thermal degradation of the nanocomposite. Testing was carried out from 30 to 600 °C under nitrogen flow at a heating rate of 10 °C/min.

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References