Structure and Mechanical Properties of Carboxylated Styrene-Butadiene Rubber (XSBR)/Pristine Clay Nanocomposites

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Abstract: Carboxylated styrene-butadiene rubber (XSBR)/clay nanocomposites were prepared by mixing the XSBR latex with aqueous clay dispersion and co-coagulating the mixture. TEM and XRD were applied to characterize the structure of nanocomposites. Fully exfoliated structure was observed for the nanocomposites containing equal to or less than 10 phr (weight parts per hundred) clay. With increasing the clay content to 20 phr, both non-exfoliated (stacked layers) and exfoliated structures can be observed simultaneously in the nanocomposites. The results of mechanical tests on the vulcanized clay-free XSBR and XSBR/clay nanocomposites showed that the nanocomposites present better mechanical properties than clay-free XSBR vulcanizate. Furthermore, modulus, tensile strength, tensile strain at break and hardness (shore A) increased with increasing the clay content, indicating the nanoreinforcement effect of clay on the mechanical properties of XSBR/clay nanocomposites.

Introduction

For many years, high performance elastomers have been prepared by using carbon black, which improves the mechanical property effectively, but unfortunately pollutes the environment and is derived from petroleum. Introduction of a small amount of nanoclay into a polymer matrix improves a variety of properties such as mechanical and barrier properties. Recently, polymer/clay (layered silicate) nanocomposites have attracted much attention for both academic research and industrial applications because they generally present unexpected properties synergistically obtained from the two components [1-2]. The essence of this development is the nanoscale dispersion [3-4] and the very high aspect ratio of the clay layers [5]. Nowadays rubber/clay nanocomposites are of great interest because of their excellent gas barrier properties and, more importantly, their much higher relative strength in comparison with plastics/clay nanocomposites [6]. For example, when 5 phr organoclay was used to reinforce styrene-butadiene rubber (SBR), the tensile strength was improved from 2 to 3.7 MPa, while for polypropylene filled with 5 phr organoclay the tensile strength only increased from 32 to 35.8 MPa [7].

Different methods have been used to prepare rubber/layered silicate nanocomposites such as acrylonitrile-butadiene rubber (NBR) [8], ethylene-propylene-diene monomer (EPDM) [9], polyurethane (PU) rubber [10, 11], natural rubber (NR) [12], butadiene rubber (BR) and SBR [13-17]. Generally, in situ polymerization, solution and melt intercalation are the preparation methods of rubber/clay nanocomposites, wherein
organic modified layered silicate must be used. However, considering that the latices are aqueous polymer dispersions and water is an excellent exfoliating agent for pristine clays, co-coagulating the mixture of rubber latex and layered silicate aqueous suspension (latex compounding method) is an easy method to prepare layered silicate/ rubber nanocomposites wherein pristine clay, i.e. sodium montmorillonite (Na-MMT), is used instead of organic clay [13-14, 18-19].

XSBR latices are among the most important polymeric colloids, which are used as binder in paper coatings, carpet backing, paints and non-wovens. Barrier properties of the nanocomposites of NR, XSBR and their blends prepared by latex compounding method have been investigated [20, 21]. Layered silicates (sodium bentonite and sodium fluorohectorite) have been used as the nanofillers. Due to the enhanced polymer/nanofiller interaction, the nanocomposites exhibited lower permeability to oxygen and nitrogen gases. The platelet structure of layered silicates has the ability to improve the barrier properties of polymer materials according to a tortuous path model [21] in which a small amount of layered silicates reduce significantly the permeability of gases through the nanocomposites. Stephan et al. have recently investigated the transport properties of nanostructured layered silicate (sodium bentonite or sodium fluorohectorite) reinforced NR, XSBR and their 70/30 blends by equilibrium swelling method using benzene, toluene and \( \rho \)-xylene [22]. The nanocomposites exhibited reduced absorption rate. This is because of increased polymer/filler interaction, which resulted in tortuosity of path and the reduced transport area in polymeric membrane. Moreover, solvent resistance of the nanocomposites increased with amount of layered silicate due to the confinement of the chain segments between the layers of layered silicates. Aqueous dispersions of organically modified boehmite nanoparticles have been mixed with XSBR latex [23]. After water evaporation, homogeneous (nano)composites were obtained when the modifier (acrylic acid or diethyl phosphoric acid) concentration was in the range of 0.5-3 wt%. Improved mechanical properties were observed for the nanocomposites.

In the present work, XSBR/ pristine clay nanocomposites were prepared by co-coagulating the mixture of rubber latex and clay aqueous suspension. Structure and mechanical properties of the nanocomposites were studied in detail. TEM and XRD were used for investigating the structures of XSBR/ clay nanocomposites.

Results and Discussion

Structure of XSBR/ clay nanocomposites

Qualitative understanding of the structure of nanocomposite through direct observation can be achieved by TEM observation. On the other hand, XRD is a conventional method to determine the interlayer spacing of clay layers in the original clay and in the polymer/layered silicate nanocomposite. The XRD patterns of the XSBR/ Na-MMT nanocomposites and pure Na-MMT powder are presented in Fig. 1. Results in Fig. 1 suggest that in the nanocomposites prepared with equal to or less than 10 phr Na-MMT, silicate layers may be completely exfoliated, which will be confirmed by TEM observation (see below). Also, it is clear from Fig. 1 that the measured \( d_{001} \) basal spacing of pure Na-MMT and nanocomposite with 20 phr Na-MMT are the same (1.29 nm), suggesting that the stacked layers of silicates without intercalation of rubber chains can be formed in the nanocomposites containing the high clay loading.
TEM micrographs of the XSBR/clay nanocomposites are shown in Fig. 2. The dark regions are the hard layered silicates while the light regions are the soft rubber matrix [25-26]. Clearly, the Na-MMT layers in the nanocomposite containing 2 phr clay (Fig. 2a) are totally separated into very fine units in the rubber matrix, i.e. single layers with an average width of about 1-2 nm (thickness of a single Na-MMT layer is about 1 nm) which is consistent with XRD result. This result is direct evidence that XSBR/Na-MMT nanocomposites have formed. The similar results were observed for the nanocomposites containing 5 and 10 phr clay (Fig. 2). On the other hand, TEM micrograph of the nanocomposite containing 20 phr Na-MMT (Fig. 2) reveals that a hybrid structure of monolayered (about 1-2 nm in thickness) and multilayered (stacked sheets with thickness larger than 2 nm) silicates can be formed simultaneously in the nanocomposite with higher clay loading. According to the TEM observations and XRD patterns observed for nanocomposite containing 20 phr Na-MMT, it was concluded that exfoliated and non-exfoliated hybrid structure can coexist in the nanocomposite containing high clay loading.

![Fig. 1. XRD patterns for the pure Na-MMT and XSBR/Na-MMT nanocomposites.](image)

SBR/Na-MMT nanocomposites have been prepared by a procedure same as that in the present study [17]. It has been observed that fully exfoliated structure of SBR/clay nanocomposites could be obtained by this method only when the 6 phr Na-MMT is used while in the present study, XSBR/Na-MMT nanocomposites containing 10 phr clay had a fully exfoliated structure. This difference may be attributed to the presence of carboxyl groups on the surface of XSBR particles, which results in the strong interaction with the surfaces of layered silicates preventing the re-aggregation of single silicate layers during the co-coagulating process (see next section and Fig. 3). In other words, the presence of polar carboxyl groups in the XSBR chains can result in the better compatibility between rubber chains and layered silicates. As a result, thermodynamically stable nanocomposites may also be formed.
It should be noted that some (not most) of clay layers are lying flat on section, i.e. their planar surfaces are along the section, as can be seen as dark regions in TEM micrographs with about 200 nm in length and about 200 nm in width. These regions were shown in TEM micrographs. Strong shear during processing causes a serious breakage of dispersed layered silicates considering its original micro-scale length and width, just like that reported in the literature [18, 27]. However, most of clay layers can be observed as the cross-section of single layers with thickness of about 1-2 nm. The thickness of some clay layers in Figs. 2b and 2c is higher than that of a single Na-MMT layer, which is about 1 nm. This has also been observed in the literature [28, 29] and possible reasons are follows. First, the cross-section of single layers may not be perfectly normal to the surface of the TEM observation and therefore the micrograph shows tilted platelets that appear thicker. Second, there is

Fig. 2. TEM micrographs of the XSBR/clay non-vulcanized compounds containing (a) 2 phr, (b) 5 phr, (c) 10 phr and (d) 20 phr Na-MMT.
always the possibility of imperfect focusing of these unstable samples, in the TEM [28]. So, it is seems to be correct to point the exfoliated and non-exfoliated (stacking sheets without intercalation) based on the TEM micrographs.

Fig. 3. Schematic illustration of the mixing and co-coagulating processes [27].

If intercalation of rubber chains into the interlayer of clay occurs, XRD peak will shift to a smaller angle for the intercalated nanocomposites, and if the Na-MMT layers are exfoliated completely, there will be no diffraction peaks observed because of the disorder of sheets or the larger space of the layers beyond the XRD resolution. In this study, the $d_{001}$ basal spacing of the nanocomposite containing 20 phr clay was same as that of pure Na-MMT powder, which would be too small for intercalation of rubber molecules into the space of Na-MMT. This nanodispersed structure without polymer chains intercalated into the silicate layers is completely different from the well-known intercalated structure and exfoliated structure, which is apparently due to the unique preparation method. This has been investigated completely by Wang et al [27] as shown in Fig. 3. Based on the above results and Fig. 3, the dispersion phase of the nanocomposites prepared by latex compounding method involves the single (exfoliated) layer and nanoscale orderly stacking (non-exfoliated) layers without polymer inserted between the layers. It is clear from Fig. 3 that the non-exfoliated stacking layers in the rubber/clay nanocomposites prepared by co-coagulation of the mixture of rubber latex and aqueous clay suspension are formed by the re-aggregation of single clay layers during the co-coagulating process.

**Mechanical Properties of XSBR/Clay nanocomposites**

Fig. 4 shows the mechanical properties of XSBR/clay nanocomposites. The hardness (shore A) and 100% modulus (i.e. modulus at 100% elongation) of nanocomposites (Fig. 4a) are higher than those of clay-free XSBR vulcanizate and also increased with increasing the amount of clay. It can be attributed to the layered structure of clay and extremely high interfacial action between the silicate layers (or stacked layers) and rubber matrix. Fig. 4b shows that the tensile strength and tensile strain at break of XSBR is improved by introducing the clay into the rubber matrix. In addition, the improvement is increased by increasing the amount of clay in nanocomposites.
**Fig. 4.** Mechanical properties of clay-free XSBR vulcanizate and XSBR/Na-MMT nanocomposites.

The significant improvements of mechanical properties may give the evidence that both exfoliation and a large interface play critical roles in nano-reinforcement. It should be noted that all of the mechanical properties of nanocomposites improve considerably with increase in the clay content up to 10 phr and then become less important, which is consistent with the structure of nanocomposites observed by TEM and XRD. In other words, maximum improvement in the mechanical properties of nanocomposites can be achieved only when the all of layered silicates separate into the single layers.

**Conclusions**

XSBR/clay nanocomposites were prepared by co-coagulating the mixture of XSBR latex and aqueous clay suspension. TEM and XRD were used to investigate the structure of nanocomposites. It was observed that the fully exfoliated structure could be obtained by this method when the content of layered silicates is equal to or less than 10 phr. It was proposed that the presence of polar carboxyl groups in the XSBR chains can result in the better compatibility between rubber chains and layered silicates. The nanocomposites have the higher hardness (shore A), 100% modulus,
tensile strength and tensile strain at break than the clay-free XSBR vulcanizate, which resulted from the nano-reinforcement effect of clay. On the bases of TEM observation, XRD analysis and mechanical properties, it was concluded that maximum improvement in the mechanical properties could be achieved when the layered silicates separated (fully exfoliated) into the single layers.

Experimental

Materials

Cloisite Na⁺ (natural sodium-montmorillonite, Na-MMT) as a pristine clay with cation exchange capacity of 92 meq/100 g of clay was provided by Southern Clay products. XSBR latex with 30% solid content and mean diameter (measured by dynamic light scattering) of 263.2 nm was prepared according to the literature [24] by emulsion copolymerization of styrene (St), butadiene (Bu) and acrylic acid (AA) in the presence of sodium lauryl sulfate (SLS) as an emulsifier and potassium persulfate (KPS) as an initiator (Table 1). Reaction time and conversion was 10 h and 99.76% respectively. The rubber additives such as zinc oxide, stearic acid, sulfur etc were of commercial grade.

Preparation of XSBR/clay nanocomposites

Clay (Cloisite Na⁺) was dispersed in deionized water with vigorous stirring by a special type of stirrer (Polytron, Switzerland) at a concentration of 2 wt% and an aqueous suspension of layered silicate was obtained. Then, a given amount of XSBR latex was added into the aqueous clay suspension and stirred for 30 min. Finally, the mixture was co-coagulated by cation-type coagulating agent (dilute solution of calcium chloride, 2%), washed with water several times and dried at 80 °C for 24 h under reduced pressure. The XSBR/clay mixture were then obtained.

Tab. 1. Emulsion copolymerization of styrene- butadiene- acrylic acid by initial charge process at 70 °C [24].

<table>
<thead>
<tr>
<th>Components</th>
<th>amounts (phmᵃ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>St</td>
<td>57.60</td>
</tr>
<tr>
<td>Bu</td>
<td>38.40</td>
</tr>
<tr>
<td>AA</td>
<td>4.00</td>
</tr>
<tr>
<td>SLS</td>
<td>2.35</td>
</tr>
<tr>
<td>KPS</td>
<td>0.82</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>228.00</td>
</tr>
</tbody>
</table>

ᵃ parts per hundred monomers.

To obtain the vulcanized nanocomposites for mechanical tests, the above-mentioned mixtures as well as the clay-free XSBR were mixed with ingredients according to the recipe in Table 2 in a 6-inch two-roll mill. Firstly, rubber containing various amount of Na-MMT (0-20 phr) was compounded with DOP, ZnO and stearic acid for 6 min at 60-70 °C. Then, accelerators, sulfur and antioxidant were added respectively to the mixture. Approximately 50 g of rubber compound were vulcanized in a standard mold.
(2 mm × 110 mm) at 20 ton pressure and 150 °C for the optimum cure time determined by a rheometer. The vulcanizates are referred to as XSBR/ Na-MMT nanocomposites.

**Characterization of the nanocomposites**

Transmission electron microscopy (Philips CM 200 TEM, using an acceleration voltage of 200 kV) was used to map the distribution of clay platelets in the rubber matrix. X-ray diffraction (XRD) analysis was performed using a Philips Analytical X-ray diffractometer. An acceleration voltage of 40 kV and 25 mA were applied using Cu $K_\alpha$ radiation with wavelength $\lambda = 0.154$ nm. The diffraction curves were obtained within the range of scattering angles ($2\theta$) of 1-10° at a scan rate of 1°/min. It should be noted that the samples used in XRD analysis were the sheets obtained from molding while those used in TEM experiments were ultrathin films of the nanocomposites prepared by drying one drop of the aqueous mixture of XSBR latex and clay suspension on the TEM sample grid.

Tensile test on the (at least five) specimens were performed using a Zwick/ Roell Tensile tester at a stretching speed of 500 mm/min at the ambient temperature (25 °C) according to ISO 37-1994. All results except TEM observations have been achieved on the Vulcanized rubber.

**Tab. 2.** Recipe for vulcanization of XSBR/ Na-MMT compounds.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Amounts (phr$^a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XSBR</td>
<td>100</td>
</tr>
<tr>
<td>Cloisite Na$^+$</td>
<td>Variable</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>Dibenzothiazole disulfide (DM)</td>
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<tr>
<td>Tetramethyl thiuram disulfide (TMTD)</td>
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</tr>
<tr>
<td>Sulfur</td>
<td>2.0</td>
</tr>
<tr>
<td>Dioctylphthalate (DOP)</td>
<td>10.0</td>
</tr>
<tr>
<td>$N$-isopropyl-$N'$-phenyl-$p$-phenylene diamine</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$ parts per hundred rubber

**References**