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ORIGINAL PAPER

# Characterization of NBR/bentonite composites: vulcanization kinetics and rheometric and mechanical properties

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**Abstract** The effect of the incorporation of bentonite (BT) untreated and treated with octadecylamine on the rheological behavior and vulcanization kinetics of NBR was investigated. Mechanical properties were also evaluated. Decreases in the optimum cure time ($t_{90}$) and in the scorch time ($t_{S2}$) and a notorious improvement in mechanical properties were found when treated BT was employed. From the vulcanization kinetics analysis, we can infer that the curing rate is superior for the treated BT composites, while the reaction orders point out the dependency of the vulcanization reaction on the initial reactants if compared to the catalytic effect of the reaction products.

**Keywords** Acrylonitrile-butadiene rubber (NBR) composites · Bentonite · Rheological behavior · Mechanical properties · Vulcanization kinetics

## Introduction

The incorporation of fillers into elastomer matrices gives place to a significant increase in their mechanical and physical properties. This behavior is a consequence of the reinforcing effect of the filler because of the hydrodynamic interactions between the elastomer and the reinforcing material. In particular, carbon black is the reinforcing filler mostly used in the rubber industry. Nonetheless, in the last decade the use of nanofillers with a color different than black and which equally improve

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the tensile behavior of the vulcanizates has been increasing [1]. Among them, one can mention the layered clay silicates such as montmorillonite (MMt), hectorite, bentonite (BT), etc., which have been used as reinforcing nanofillers in polymers and elastomers due to their high aspect ratio and because at least one of their dimensions is in the nanometric range [2, 3]. One can cite Karger-Kocsis et al. [4], who analyzed the production methods of rubber/silicate composites, considering curing characteristics, the structure and basic properties (mechanical, thermal, and barrier). López-Manchado et al. [5] investigated blends of natural rubber with organoclay employing mechanical mixing or intercalation in the molten state and solution mixing and Hwang et al. [6] investigated the effect of treating layered silicate fillers with a surfactant to obtain an exfoliated structure and so to improve the mechanical properties of nitrile rubber (NBR) vulcanizates. Also, Yoon et al. [7] considered the modification of MMt with amine derivatives and Kim et al. [8] analyzed the behavior of three amino surface modifiers in NBR–MMt composites, concluding that the insertion of the modifier with the longest chain (octadecylamine) gives a greater increase in the interlayer distance, plus better mechanical properties. In addition, Chakraborty et al. [9] have studied the properties of sodium activated and organomodified BT (o-BT) clay–SBR rubber nanocomposites. In a recent study, Soares et al. [10] did a comparative study on NBR nanocomposites, based on two commercial organomodified MMt, and two procedures for clay dispersion (melt blending and solution intercalation).

In addition to the effect of the type and amount of filler on the mechanical properties of rubber compounds, one can also say that these properties are related to the degree of crosslinking. The vulcanization of a rubber compound involves multiple and complex reactions. So, the study of the cure reaction and its kinetics can give insight into the actual mechanism of vulcanization and its effect on the mechanical properties of rubber compounds [11–13].

Rheometric measurements are based on the principle that cross linking density is proportional to the stiffness of the rubber. Thus, the degree of conversion ($\alpha$) in a curing reaction can be determined from the viscoleastic properties measured through a rheometric test [11, 13, 14]. The $\alpha$ value can be defined as follows:

$$\alpha = \frac{(M_t - M_0)}{(M_\infty - M_0)}, \tag{1}$$

where $M_0$, $M_t$, and $M_\infty$ are the torque values at the initial curing, at curing time $t$, and at the end of the curing reaction, respectively. During the curing reaction of a rubber, there exists a period from zero time to induction time (scorch time) required for the initiation of the vulcanization. Then, the vulcanization reaction starts until a point where torque is 90–97% of the maximum value, commonly named as optimum vulcanization point. Once this point is reached, the torque can either remain constant, increase or decrease according to the type of rubber. The curing reaction, once scorch time has passed, can be modeled through differential equations with respect to time, in which the influence of temperature and vulcanization rate are separately evaluated [15], as in classical chemical reactions. Thus, the curing rate can be expressed according to the following expression:

$$\frac{d\alpha}{dt} = K(T)f(\alpha), \tag{2}$$

where $t$ is the time in seconds, $T$ is the temperature in Kelvin, and $K$ is the kinetics constant. The function $K(T)$ is described by the Arrhenius relationship. So, the kinetics of the curing reaction can be described as follows:

$$K(T) = K_0\exp(-E_a/RT), \tag{3}$$

where $K_0$ is the preexponential factor, $E_a$ is the activation energy in J/mol, and $R$ the universal gas constant. From Eqs. 2 and 3, the following expression can be obtained:

$$\frac{d\alpha}{dt} = K_0 f(\alpha)\exp(-E_a/RT). \tag{4}$$

The function $f(\alpha)$ depends on the mechanisms of the curing reaction. In a simple reaction, the function $f(\alpha)$ assumes that the conversion rate is proportional to the fraction of non crosslinked material [11]:

$$f(\alpha) = (1-\alpha)^n,\ n \geq 1, \tag{5}$$

where $n$ is the reaction order. This kind of kinetics would be represented by curve "a" in Fig. 1. A more complex form of the function $f(\alpha)$ is the autocatalytic model, described by the next expression [16]:

$$f(\alpha) = \alpha^m(1-\alpha)^n,\ 0 \leq m \leq 1,\ n \geq 1, \tag{6}$$

where $m$ also represents the reaction order. In a reaction of $n$ order, the maximum curing rate is observed at the beginning of the vulcanization reaction, when the maximum concentration of reactive groups is present; while in an autocatalytic reaction, the maximum curing rate is given for conversion degrees different than zero due to the promotion of the reaction with the appearance of the products [11]. In Fig. 1, this mechanism is represented by curve "b". However, in the case of the studies of reaction models in elastomers, it is necessary to recur to a general model which can cover any variant of the proposed kinetics. In this sense, the use of $f(\alpha)$ indicated on Eq. 6 is proposed. So, $d\alpha/dt$ shows the following expression [11, 13, 17]:

$$\frac{d\alpha}{dt} = K(T)\alpha^m(1-\alpha)^n, \tag{7}$$

where $n$ and $m$ are the reaction orders.

Based on these premises, this study has the intention of studying the influence of BT content (10–30 phr) untreated and treated with octadecylamine on the rheometric and mechanical properties, as well as on the vulcanization kinetics of acrylonitrile-butadiene rubber (NBR) composites. The variation on these properties with aging is also analyzed. It is important to highlight that in the above cited references, only small quantities of MMt are added, while in our study, 10–30 phr of BT are used. BT is low cost clay rich in MMt content and with a particle size lower

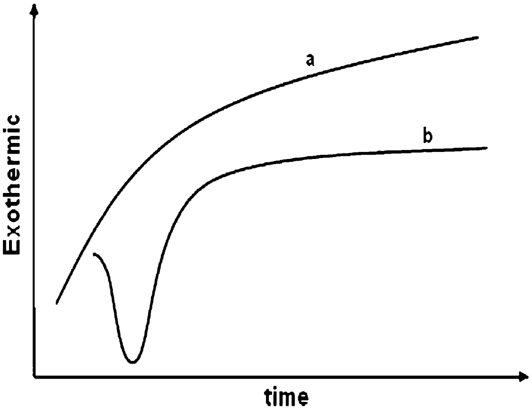

**Fig. 1** Schematic representation of curing curves according to (*a*) *n*th-order and (*b*) autocatalytic kinetics models

than 0.002 mm. Also, another motivation for the use of this clay is its high availability in the Venezuelan region of Tinaquillo, Cojedes State.

## Experimental

Composites were prepared consisting of an NBR *KRYNAC* 3345F (Lanxess, USA) with 33% acrylonitrile content and Mooney viscosity (ML, 1 + 4,100 °C = 45), and sodium bentonite OPTIBENT CP (Rockwood Additives Ltd., UK). The samples are referred as NBRxy, where x and y correspond to the amount and type of clay, respectively. Additives for all formulations were: zinc oxide (ZnO) (Zn Fundiciones C.A., Venezuela), stearic acid (Braswey S.A., Brazil), *N*-*t*-butyl benzothiazole sulfenamide (TBBS) (Suministros Químicos C.A., Venezuela) and sulfur (S) (Suministros Químicos C.A., Venezuela).

All compounds were prepared using a Banbury®internal mixer at a rotor speed of 60 rpm, following the mixing procedure reflected on the ASTM D3568 standard and according to the composition shown in Table 1. Curing characteristics and vulcanization kinetics were studied using a rotorless rheometer at 150, 160, 170, 180, and 190 °C and 0.5° oscillation according to the ASTM D5289 procedure.

**Table 1** Composition of the prepared compounds expressed in parts per hundred of rubber (phr)

| Materials | Parts per hundred of rubber (phr) |
|---|---|
| NBR | 100 |
| ZnO | 3 |
| Stearic acid | 1 |
| S | 1.5 |
| TBBS | 0.7 |
| BT | 10, 20, and 30 |

Bentonite was modified by introducing organic ions into the interlayer spacing rendering hydrophobic surfaces via ion exchange reaction. This ion exchange produces organophilic clays which are more compatible with the polymer [18].

The treatment of the BT was done through stirring in aqueous solution with octadecylamine and HCl at 500 rpm and 80 °C. After 1 h at this temperature and under vigorous stirring, the suspension was filtered and dried at 80 °C during 48 h. The resulting dried organoclay (o-BT) was grinded in a ball mill. Particle size distribution was determined by a laser diffraction technique (Malvern, Mastersizer 2000). Also, the BT particles with and without octadecylamine were characterized by means of Scanning electron microscopy (SEM, Hitachi S-2400) and by Fourier Transform Infrared Spectroscopy (FTIR) measurements. These spectra were recorded in a Nicolet Magna_IR 560 E.S.P. Spectrometer after 32 scans and at 2 $\mathrm{cm}^{-1}$ of resolution. X-ray diffraction (XRD) patterns were recorded using a diffractometer (Siemens, D 500) in the $2\theta$ range of 2°–60° and Energy-dispersive X-ray spectroscopy (EDX) was also employed to perform a quantitative analysis of the chemical composition of the clays.

Tensile and tear properties of the vulcanized blends were determined following ASTM D412 and D624 procedures, respectively. Test for hardness was carried out using a Shore type A Durometer in accordance with ASTM D2240.

The thermal aging resistance test of NBR vulcanizates was performed to determine the influence of elevated temperatures and time on the mechanical properties and on the crosslinking density of vulcanized NBR and NBR/BT composites, based on ASTM D573-88 and ASTM D2000 procedures. The dumbbell specimens were placed in a hot-air oven at a temperature of 100 °C for 72 h.

Morphological studies of cryogenically fractured samples of NBR with pristine and treated BT were carried out using SEM. The samples were fractured in liquid nitrogen and the surface covered with a thin layer of platinum–palladium.

The samples vulcanized at 170 °C were chosen for the study of the tensile behavior, the thermal aging resistance, as well as for the determination of the crosslinking density and the morphology analysis, since this temperature is commonly employed for the curing of NBR [19].

## Results and discussion

From the particle size distribution obtained for pristine BT and treated BT (o-BT) (Fig. 2), we determined that the average particle size of the BT was 71.04 µm with a specific area of 0.922 $\mathrm{m}^2$/g, while the o-BT had an average particle size of 36.7 µm and a specific area of 1.432 $\mathrm{m}^2$/g. Figure 3 shows the morphology of the untreated and treated BT particles. It can be seen that the particles tend to agglomerate regardless the nature of the clay.

Both clays were also characterized through EDX (Fig. 4) with the intention of determining the extent of modification via ion exchange reaction. Figure 4 shows that the o-BT presents a more pronounced peak for the Carbon (C) element, thus we could presume that C content is higher and that it comes from the octadecylamine.

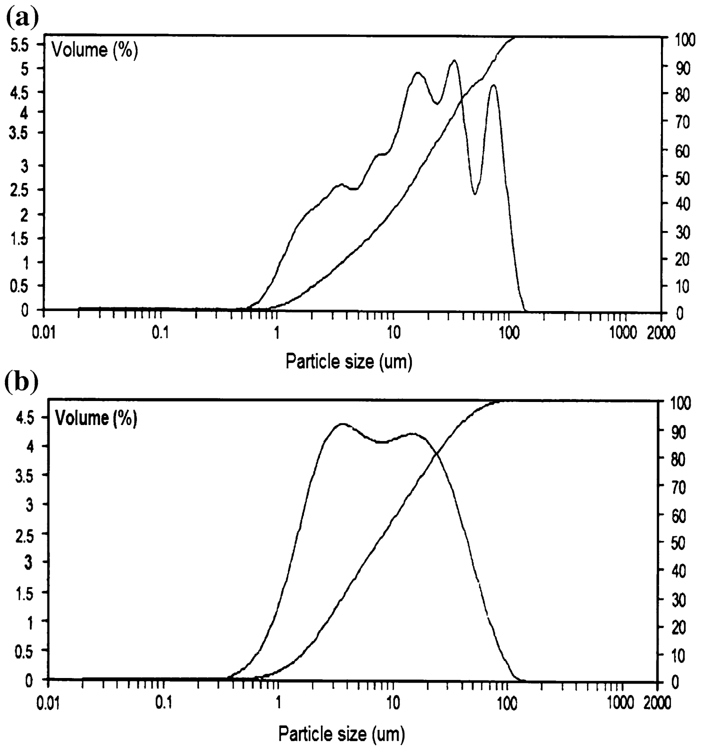

**Fig. 2** Particle size distribution of **a** untreated BT and **b** o-BT

The other peaks reflected on the spectra of the o-BT represent other characteristic elements.

In addition, XRD patterns are presented in Fig. 5 where we can notice that the BT shows a characteristic diffraction peak at $2\theta = 6.9°$, which is assigned to the interlayer platelet spacing of BT with a spacing of 14.6 Å. However, a displacement of the peak to lower angles ($2\theta = 5.4°$) is observed for the treated clay, which, as deduced by the Bragg's law equation, corresponds to an interlayer distance of 18.2 Å. According to these results, we could presume that the octadecylamine behaves as an effective intercalating agent, delaminating the BT [1, 20].

On the other hand, in the FTIR spectra exposed in Fig. 6, we can observe two peaks around 2918 and 2850 $\text{cm}^{-1}$ for the treated BT, attributed to the C–H asymmetric and symmetric stretching vibrations of octadecylamine, respectively. Also, the peak observed at 3500 $\text{cm}^{-1}$ for the pristine clay and characteristic of the OH groups appears with lower intensity. These results further indicate that the treated BT presents a hydrophobic nature and that the ammonium salt has been incorporated within the silicate layers. Similar results were obtained by López-Manchado et al. [1].

The curing characteristics of the studied materials, expressed in terms of the minimum and maximum values of the torque, $M_L$ and $M_H$, respectively, the scorch

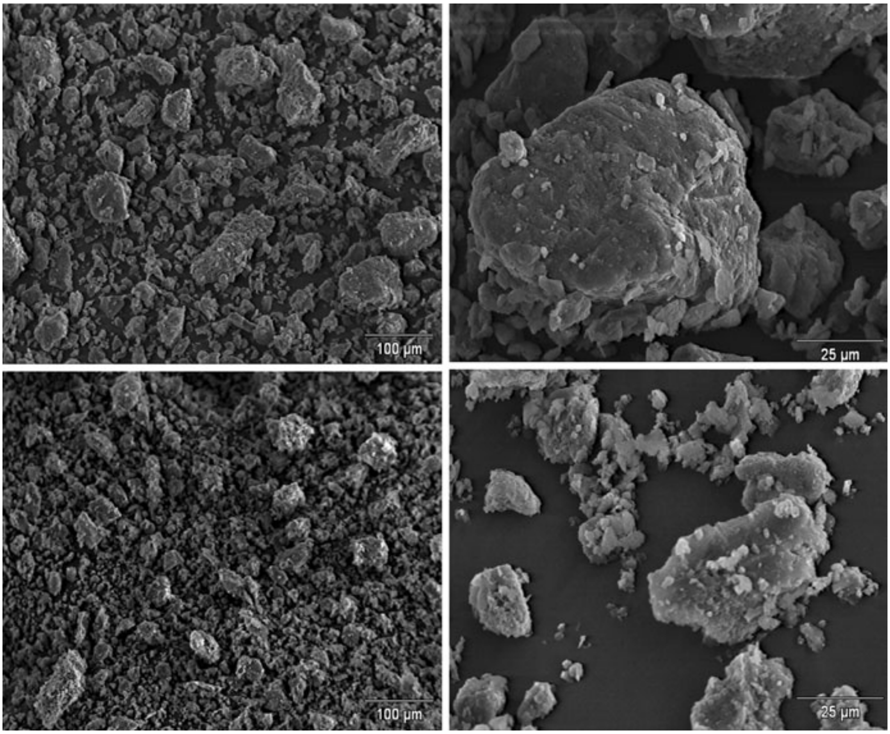

**Fig. 3** SEM microphotographs of untreated BT (*top*) and o-BT (*bottom*)

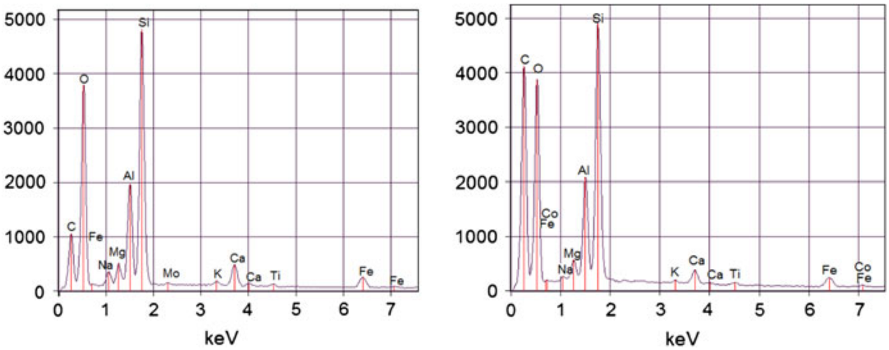

**Fig. 4** EDX analysis of untreated BT (*left*) and o-BT (*right*)

time, $t_{S2}$, the optimum cure time, $t_{90}$, and the curing rate index, CRI, are compiled in Table 2.

At a fixed temperature, the minimum torque $M_L$ which is proportional to the viscosity of the uncured compound, increases by the addition of the clay to the NBR matrix; the modification of the BT increases even more the viscosity of the system due to a higher interaction between the organoclay and the rubber.

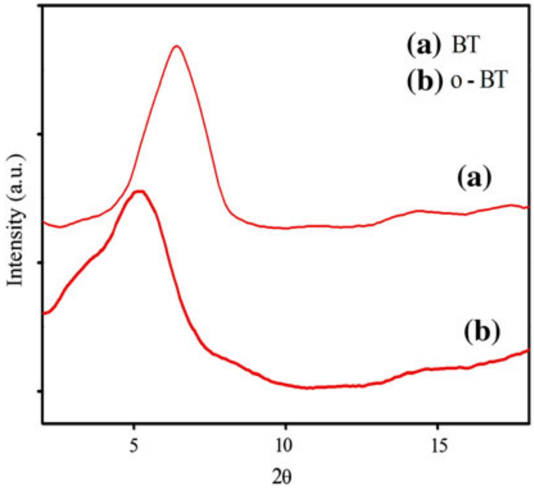

**Fig. 5** XRD diffractograms of (*a*) untreated BT and (*b*) o-BT

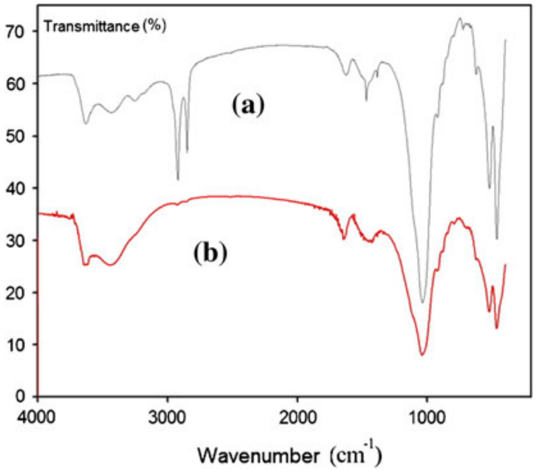

**Fig. 6** FTIR spectra of (*a*) untreated BT and (*b*) o-BT

The maximum elastic torque $M_H$ values also increase with the presence of the BT; nonetheless, the rise in this parameter for the formulations with the treated filler is less significant. In general, the presence of fillers restricts deformation, and consequently, the composite becomes harder and stiffer thereby increasing the torque of the vulcanizates. The effect of temperature on $M_L$ and $M_H$ can also be analyzed from the results shown in Table 2, where we can clearly see that both parameters decrease with increasing temperature.

Scorch time $t_{S2}$ decreases notoriously when BT is used as filler and decreases even more when the treated BT is employed probably due to the basic nature of this filler that is potentially increased with the treatment with octadecylamine. It is known that a basic medium has an activating effect on the vulcanization reaction, since amine groups and sulfur form a transition metal complex [4]. In this case, we can assume that the organoclay behaves as an effective vulcanizing agent for NBR.

**Table 2** Curing characteristics of composites at different temperatures

| Composites | Temperature (°C) | $M_L$ (dN m) | $M_H$ (dN m) | $t_{S2}$ (min) | $t_{90}$ (min) | CRI ($s^{-1}$) |
|---|---|---|---|---|---|---|
| NBR | 150 | 0.30 | 6.50 | 7.1 | 23.9 | 0.10 |
| | 160 | 0.30 | 6.48 | 4.0 | 13.2 | 0.18 |
| | 170 | 0.27 | 6.49 | 2.4 | 8.2 | 0.28 |
| | 180 | 0.26 | 6.12 | 1.5 | 4.8 | 0.52 |
| | 190 | 0.23 | 5.85 | 1.2 | 4.4 | 0.52 |
| NBR10BT | 150 | 0.51 | 8.20 | 4.8 | 22.2 | 0.10 |
| | 160 | 0.44 | 8.13 | 2.7 | 13.2 | 0.16 |
| | 170 | 0.36 | 7.73 | 1.8 | 11.0 | 0.18 |
| | 180 | 0.37 | 7.62 | 1.2 | 5.8 | 0.36 |
| | 190 | 0.38 | 7.28 | 0.9 | 3.5 | 0.65 |
| NBR20BT | 150 | 0.53 | 8.91 | 4.4 | 24.3 | 0.08 |
| | 160 | 0.49 | 8.73 | 2.5 | 15.1 | 0.13 |
| | 170 | 0.45 | 8.83 | 1.6 | 10.5 | 0.19 |
| | 180 | 0.40 | 8.27 | 1.1 | 6.1 | 0.34 |
| | 190 | 0.40 | 7.79 | 0.8 | 3.7 | 0.58 |
| NBR30BT | 150 | 0.47 | 8.97 | 6.1 | 27.9 | 0.08 |
| | 160 | 0.50 | 9.22 | 2.3 | 16.1 | 0.12 |
| | 170 | 0.53 | 10.25 | 1.4 | 10.5 | 0.18 |
| | 180 | 0.49 | 9.66 | 0.9 | 5.9 | 0.33 |
| | 190 | 0.48 | 9.23 | 0.7 | 3.5 | 0.59 |
| NBR10o-BT | 150 | 0.42 | 6.61 | 2.6 | 20.1 | 0.10 |
| | 160 | 0.41 | 6.63 | 1.7 | 10.5 | 0.19 |
| | 170 | 0.39 | 6.52 | 1.2 | 6.4 | 0.32 |
| | 180 | 0.39 | 5.89 | 0.9 | 3.8 | 0.57 |
| | 190 | 0.36 | 5.65 | 0.8 | 2.5 | 0.96 |
| NBR20o-BT | 150 | 0.64 | 7.20 | 1.8 | 18.2 | 0.10 |
| | 160 | 0.70 | 7.38 | 1.1 | 9.2 | 0.21 |
| | 170 | 0.53 | 6.57 | 0.9 | 6.4 | 0.30 |
| | 180 | 0.62 | 6.33 | 0.7 | 3.5 | 0.61 |
| | 190 | 0.60 | 5.76 | 0.6 | 2.2 | 1.04 |
| NBR30o-BT | 150 | 0.85 | 7.78 | 1.5 | 17.8 | 0.10 |
| | 160 | 0.91 | 8.20 | 1.0 | 8.6 | 0.22 |
| | 170 | 0.88 | 7.06 | 0.7 | 4.2 | 0.48 |
| | 180 | 0.90 | 6.75 | 0.6 | 3.1 | 0.67 |
| | 190 | 1.25 | 6.88 | 0.5 | 1.9 | 1.22 |

The time corresponding to 90% of the maximum torque $t_{90}$ generally increases for the composites with the pristine clay with respect to the value presented for the unfilled NBR. All these variations on the values of $t_{S2}$ and $t_{90}$ are in agreement with the results obtained by Essawy and El-Nashar [21], when montmorillonite was used as reinforcing filler in NBR/SBR rubber blends. It is also observed that $t_{S2}$ and $t_{90}$

**Table 3** Mechanical and physical properties of NBR/BT composites vulcanized at 170 °C

| Composites | $\sigma_{100}$ (MPa) | $\sigma_{300}$ (MPa) | $\sigma_B$ (MPa) | $\varepsilon_B$ (%) | TS (kN/m) | Hardness (Shore A) | $\upsilon \times 10^6$ (mol/kg) |
|---|---|---|---|---|---|---|---|
| NBR | 1.1 (0.1) | 2.0 (0.1) | 2.7 (0.3) | 421 (34) | 20 (1) | 42 (1) | 2.99 (2.54) |
| NBR10BT | 1.4 (0.1) | 2.7 (0.2) | 3.7 (0.3) | 396 (36) | 25 (1) | 44 (2) | 3.54 (0.74) |
| NBR20BT | 1.4 (0.1) | 2.7 (0.1) | 5.2 (0.5) | 538 (30) | 34 (2) | 47 (1) | 4.40 (0.50) |
| NBR30BT | 1.7 (0.1) | 3.4 (0.1) | 4.7 (0.2) | 426 (28) | 29 (2) | 50 (2) | 2.30 (1.80) |
| NBR10o-BT | 1.3 (0.1) | 2.2 (0.1) | 8.0 (0.8) | 735 (27) | 33 (1) | 45 (1) | 4.01 (0.41) |
| NBR20o-BT | 1.6 (0.1) | 2.9 (0.2) | 7.8 (0.8) | 667 (43) | 38 (3) | 51 (1) | 5.77 (0.49) |
| NBR30o-BT | 2.1 (0.1) | 3.7 (0.2) | 10.8 (0.9) | 730 (37) | 47 (2) | 58 (1) | 6.23 (0.33) |

decrease when temperature increases for the blends under study. Besides, we can notice that for the same filler content, the composites with the modified BT present a curing time lower (approximately half) than their equivalent formulation with the untreated filler, since the organophilic clay accelerates the vulcanization process, confirming their effectiveness as vulcanizing agents for NBR.

With respect to the CRI, it is observed that this parameter decreases for the composites with pristine BT, while it increases for the composites with the organoclay with respect to the value of unfilled NBR. This effect is more notorious at higher vulcanization temperatures [13]. This rise on the precocity and CRI is supported by the inclusion of the treated BT, which changes the rate of curing by participating in the cure reaction and promoting the intercalation of the octadecylamine in the silicate galleries. The CRI is a parameter proportional to the average slope of the curing rate in the step region ($100/(t_{90}-t_{S2})$). Similar results were obtained by López-Manchado et al. [5] when using octadecylamine-modified clay in NR, attributing this behavior to a synergetic effect between the filler and the amine.

Concerning the mechanical behavior of the NBR/BT composites herein studied, Table 3 shows the tensile properties of the vulcanizates at 170 °C. It is possible to observe that, in general, the BT in the proportions used acts as a reinforcing filler since it increases the tensile stress at 100% ($\sigma_{100}$) and at 300% ($\sigma_{300}$) of elongation and tensile strength and the elongation at break ($\sigma_B$ and $\varepsilon_B$, respectively), as well as the tear strength (TS).

However, the improvement when the BT is treated is far more notorious. It should be reminded that the BT was organically modified through the intercalation with octadecylamine to provide it with a hydrophobic nature, thus reducing the surface energy and increasing the surface activity and the interlayer distance as shown in the XRD pattern presented in Fig. 5. So, we can presume that the treated BT is more compatible with the rubber, and also, when the separation between silicate layers is increased, the penetration of the elastomer is easily done, thus increasing the rubber–filler interaction, as well as the reinforcing effect of the BT. This increased strength takes place without any loose in the elongation at break of the material. Moreover, a rise in elongation at break of the NBR/o-BT composites if compared to their equivalents with BT is appreciated.

The tendencies reported on the mechanical properties can be easily understood when we study the morphology of the compounds hereby considered. With respect to the morphology of the vulcanized NBR, the microphotograph shown in Fig. 7a presents a smooth fracture surface, with particulates corresponding to the different additives present in the vulcanizate. On the contrary, Fig. 7b displays a microphotograph of the NBR30BT composite, where we can clearly see an irregular surface with voids derivatives of the cavitation of the BT particles from the elastomeric matrix, after the cryogenic fracture of the samples. This fact could point out that the untreated BT has a poor adhesion with the polymer matrix due to its hydrophilic nature. As a comparison, the morphology of the NBR30o-BT compound is presented in Fig. 7c. In this case, we can detail a minimum amount of holes, as an indicative of a better adhesion of the organoclay to the rubber, thus facilitating the interaction between the filler and the NBR matrix. Besides, we can notice when comparing Fig. 7b and c that the size of the o-BT aggregates are lower than the corresponding aggregates for the pristine clay, thus corroborating the mechanical behavior obtained. Moreover, the particle size of the BT aggregates in the composites (Fig. 7b, c) is lower than the particle size distribution that was determined by laser diffraction techniques (Fig. 2). Therefore, we could presume that desegregations of the clay took place during the mixing stage of the elastomer with the filler, thus improving the dispersion, especially when the filler was treated.

Regarding hardness values, it can be seen in Table 3 that the presence of the clay in the NBR matrix increases this property, acting like rigid filler and increasing the

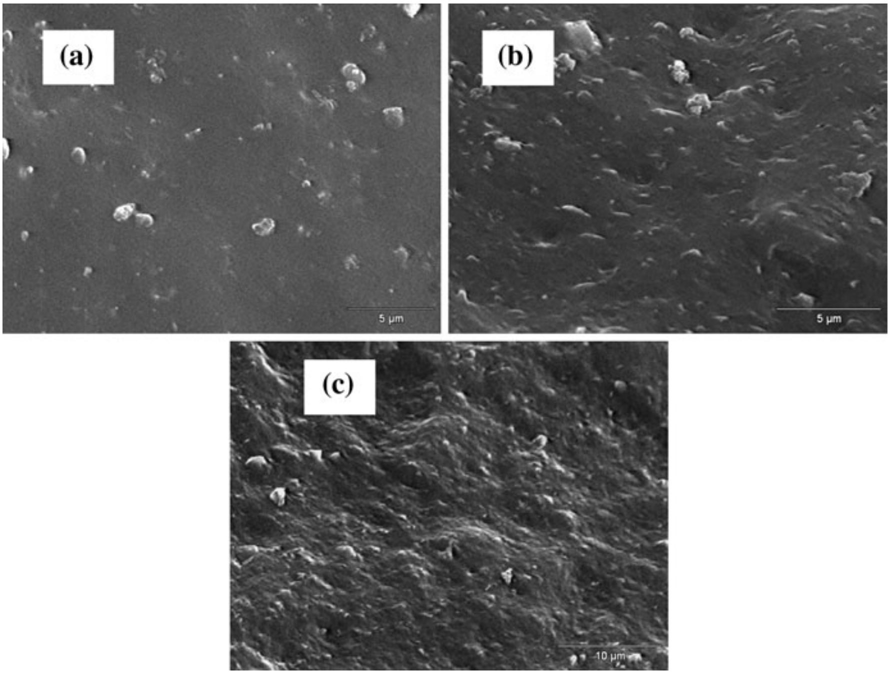

**Fig. 7** SEM microphotographs of **a** vulcanized NBR; **b** NBR30BT; and **c** NBR30o-BT

strength of the composite. This rise is more notorious when the filler added has been treated since a higher crosslinking degree is achievable (see Table 3). The crosslinking density increases with the presence of the organoclay, probably due to the interactions between the clay and the cure system as previously discussed, as well as to the compatibility between both phases which does allow the formation of additional crosslinks.

The aging characteristics of the NBR/BT composites were also evaluated. ASTM D2000 standard points out that for compounds with classification cell “BF”, just as NBR, the maximum permitted changes due to aging are ±30% for tensile properties, −50% for the elongation at break, and ±15 units for hardness. In Table 4, the variations obtained in mechanical and physical properties of the NBR/BT composites are reported. It can be appreciated that almost all values are between the specified variation ranges. Interestingly, the good aged properties of the NBR/organoclay composites could also be related to an enhanced thermal stability of the systems where the polymer chains penetrate into the galleries of the clay, giving rise to exfoliation of the silicate nanolayers [1]. Besides, the clay could prevent out-diffusion of the volatile decomposition products. Nevertheless, more detailed and systematic study on the thermal properties of these systems will be further published.

We can also say that the diminution in tensile strength, elongation at break, and TS after aging (Table 4) are similar to the results reported by Liu et al. [22] in nanocomposites of NBR and organomodified MMT treated with hexadecyltrimethyl ammoniun bromide. Moreover, from the results presented in Table 4, we can observe that the tensile stress at 300% ($\sigma_{300}$) after aging increases with the presence of 20 phr of BT, in accordance with the higher values of crosslinking density (Table 3), as indicated by Das et al. [23]. These authors suggest that during aging, residual curing occurs, and consequently, the crosslinking density increases which is reflected in higher tensile stress values. In our research, this residual crosslinking seems to be more prominent in the presence of o-BT.

In order to study the kinetics of the curing reaction, the curing torque was measured at different temperatures. Table 5 shows the vulcanization kinetics of NBR composites. It is seen that the $K$ values are higher for the compounds with treated BT when compared to the compounds with the pristine clay, indicating that

**Table 4** Variation on the mechanical properties of NBR/BT vulcanizates after aging at 100 °C during 72 h

| Composites | $\Delta\sigma_{300}$ (%) | $\Delta\sigma_B$ (%) | $\Delta\varepsilon_B$ (%) | ΔTS (%) | ΔShore A |
|---|---|---|---|---|---|
| NBR | +27 | +4 | −19 | −13 | +2 |
| NBR10BT | −14 | −16 | −4 | −30 | +3 |
| NBR20BT | +32 | −16 | −32 | −17 | +2 |
| NBR30BT | −4 | −11 | −8 | −11 | +3 |
| NBR10o-BT | +27 | −36 | −39 | −29 | +3 |
| NBR20o-BT | +30 | −4 | −20 | −7 | +2 |
| NBR30o-BT | +23 | −15 | −23 | −10 | +3 |

**Table 5** Kinetics parameters of NBR/BT vulcanizates

| Composites | $T$ (°C) | $K$ | $n$ | $m$ | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| NBR | 150 | 0.018 | 3.01 | 0.81 | |
| | 160 | 0.030 | 2.78 | 0.78 | |
| | 170 | 0.045 | 2.62 | 0.77 | 55.7 |
| | 180 | 0.060 | 2.29 | 0.73 | |
| | 190 | 0.070 | 2.41 | 0.71 | |
| NBR10BT | 150 | 0.021 | 3.11 | 0.83 | |
| | 160 | 0.033 | 2.97 | 0.78 | |
| | 170 | 0.028 | 2.76 | 0.57 | 49.1 |
| | 180 | 0.058 | 2.57 | 0.67 | |
| | 190 | 0.073 | 2.21 | 0.65 | |
| NBR20BT | 150 | 0.020 | 3.42 | 0.81 | |
| | 160 | 0.027 | 3.19 | 0.71 | |
| | 170 | 0.034 | 3.00 | 0.59 | 48.5 |
| | 180 | 0.055 | 2.75 | 0.63 | |
| | 190 | 0.064 | 2.24 | 0.58 | |
| NBR30BT | 150 | 0.011 | 3.07 | 0.68 | |
| | 160 | 0.014 | 2.80 | 0.45 | |
| | 170 | 0.035 | 3.12 | 0.58 | 48.8 |
| | 180 | 0.044 | 2.59 | 0.53 | |
| | 190 | 0.056 | 2.15 | 0.50 | |
| NBR10o-BT | 150 | 0.032 | 3.73 | 0.66 | |
| | 160 | 0.055 | 3.36 | 0.68 | |
| | 170 | 0.089 | 3.18 | 0.77 | 43.0 |
| | 180 | 0.101 | 2.68 | 0.75 | |
| | 190 | 0.112 | 2.25 | 0.70 | |
| NBR20o-BT | 150 | 0.037 | 3.80 | 0.60 | |
| | 160 | 0.057 | 3.25 | 0.64 | |
| | 170 | 0.072 | 3.13 | 0.63 | 43.2 |
| | 180 | 0.078 | 2.42 | 0.54 | |
| | 190 | 0.087 | 2.05 | 0.50 | |
| NBR30o-BT | 150 | 0.035 | 3.70 | 0.58 | |
| | 160 | 0.050 | 3.04 | 0.58 | |
| | 170 | 0.044 | 2.13 | 0.35 | 40.3 |
| | 180 | 0.062 | 2.16 | 0.40 | |
| | 190 | 0.057 | 1.50 | 0.20 | |

the curing rate is superior. This behavior is a consequence of the smaller particle size and better dispersion of the treated clay in the NBR matrix, as previously shown. When we analyze the data of $n$ and $m$, we can say that in a reaction of order $n$ the maximum rate of cure is observed at the beginning of the vulcanization process, when the concentration of all reactants is maximum; while in an autocatalytic reaction, the maximum rate of cure is given by a conversion degree different from zero since the reaction is promoted by the appearance of the products. With regard to the non-catalytic reaction order *n*, we can observe that they slightly decrease with the temperature rise, situating themselves between 2.0 and 3.8, for all the composites, being the values to some extent higher for the composites with treated BT. On the other hand, the *m* values, representing the catalytic reaction, are lower than the unit and decrease with temperature, being fairly lower for the composites with the modified BT. This behavior could be indicating that when treated BT is employed as filler in NBR compounds, the vulcanization reaction is less autocatalytic. Also, the fact that the *n* values are higher than the *m* values points out the dependency of the vulcanization reaction on the initial reactants of the compound if compared to the catalytic effect of the reaction products. In addition, the fractioned values of *n* and *m* indicate that the vulcanization process cannot be represented by a simple elemental reaction, but by various reactions which can occur simultaneously or in series.

With respect to the activation energy ($E_a$), we can see in Table 5 that it lies between 49–48 kJ/mol and 43–40 kJ/mol for the composites with untreated and treated BT, respectively, being all values lower than the $E_a$ obtained for the neat NBR (55 kJ/mol). The lowest values obtained for the NBR/organoclay confirm that the modified BT accelerates the curing reaction of the NBR.

## Conclusions

The addition of BT to NBR vulcanizates promotes a decrease in the scorch time and an increase in the curing time of the vulcanization reaction. However, the treatment of the filler with octadecylamine decreases both parameters, thus considerably increasing the CRI of the NBR. Concerning the mechanical behavior of these vulcanizates at 170 °C, the results obtained let us consider the BT as reinforcing filler for the NBR since the tensile strength and the TS increase. The BT organically modified through the intercalation with octadecylamine increases even more this tendency due to the greater compatibility with the rubber and to a finer and more homogenous morphology.

From the vulcanization kinetics analysis, we can infer that the curing rate is superior for the treated BT composites, while the reaction order values point out the dependency of the vulcanization reaction on the initial reactants if compared to the catalytic effect of the reaction products. Thus, as a final conclusion we can say that NBR/organoclay composites show the lower activation energy values and the higher crosslinking degree which not only will shorten the vulcanization process but will give rise to improved physical properties in the NBR composites as shown along this study.

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