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# Characterization of Mechanical and Thermal Properties of Poly(ethylene-*co*-vinyl acetate) with Differents Bentonites

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**Summary:** In this study, poly(ethylene-co-vinyl acetate) (EVA) with different organophilic bentonites were prepared by melt-blended and evaluated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and the tensile properties. The results showed that the modification of bentonite with the two different surfactants presented distinct thermal and tensile behaviors of the samples containing natural bentonite. Both modifiers acted on the compatibility of the filler with the polymer matrix, obtaining injected-specimens that were visibly homogeneous. The samples containing the Cloisite® bentonite modified with ammonium salt-free surfactant (eBI-AM) presented a different behavior from the others, in that increased crystallinity, which was verified through DSC, due to the nucleating effect of the filler influenced the flexible character of the EVA materials, thus increasing the rigidity and decreasing elongation. Therefore, it was of utmost importance the use and the proposal of an ammonium salt-free modifier due to the low thermal stability that are caused by them in polymer/organophilic bentonite, as it has already been reported in the literature.

**Keywords:** bentonites; clay; mechanical properties; organophilic bentonite; poly(ethylene-co-vinyl acetate)

## Introduction

Polymer composites are formed by the presence of inorganic or organic fillers dispersed in the polymer, and they can be presented in the shape of spheres, threads or fibers, particulates, and so forth. The size of these fillers is the main property determining the behavior of these composites. The use of fillers with at least one of the nanometric dimensions forms the so-called nanocomposites. The natural and inorganic fillers, in nanometric scale, that are most commonly used are clay minerals because, when they are modified, they promote a synergic effect on the processability and in the final properties of the materials, such as tensile strength, thermal stability, and barrier to gas.[1–4] The dispersion of nanometric fillers on polymers is greatly impaired due to the incompatibility with the organic matrix. Because it presents a high ratio of aspects and a hydrophilic surface, natural clay minerals are usually modified using surfactants.[5–8] The aspect ratio of a clay mineral is the relation between the length and the diameter of the layered, thus, the higher the value of the relation, smaller is the diameter, and more differentiated will the properties exerted by the materials be. The presence of structures of surfactants such as ammonium quaternary salts gives the organic material a more hydrophobic character, allowing compatibility with polymer matrices. The main feature, and therefore the most exploited one, in clay

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minerals such as montmorillonite (MMT), which is present in bentonites at 70% to 90% concentrations, is the presence of exchangeable ions in the interlamellar region or galleries, which is also known as interlamellar spacing.[9–10] This region is formed once the MMT presents a well-defined structural arrangement that is constituted by layered or successive layers of the 2:1 type, that is, two tetrahedral sheets comprised of silicon-oxygen links and a central octahedral sheet comprised by links of aluminum atoms connected to the oxygen atoms present on the tetrahedral sheets, forming the layers with a depth ranging up to 9 Å and a basal spacing around 15 Å. In the case of MMT, around 80% of the exchangeable cations are located in this region and the rest are on the lateral surfaces. It is from this property that the so-called organophilic clays are produced, using organic molecules between structural layers or adsorbed on the surfaces. In the case of quaternary ammonium salts, they are used in the modification and in general have one or two groups of long-chain hydrocarbons in (derived from fatty acids) directly linked to one nitrogen atom where the cationic part of the molecule is located. The ammonium salts, when added to aqueous dispersions containing clay minerals replace the sodium cations that are easily changeable, thus the ammonium cations, with their long free hydrocarbon chains accommodating between the layers of clay mineral, turning them into organophilic.[11] However, the presence of the ammonium salts in the nanocomposites promotes disadvantages because of their low thermal stability.[12] An alternative to this was to evaluate another type of modifier to the clay minerals and apply them in polymer matrix.[13] The study concerning the properties exerted by organophilic clays on polymers is extremely relevant in academic research, also being accessible and applicable to the industrial sector. One example is the use of nanocomposites with poly(ethylene vinyl-co-acetate) (EVA) containing organophilic clays in wires and cables.[14] The presence of organophilic clays promotes a synergy in the polymer matrix, allowing the prepared material to present a fire-delaying effect, therefore reducing the inflammability of the polymer, in addition to the gas barrier, which hampers mainly the permeation of water vapor and oxygen.

This study consisted in the preparation and evaluation of the thermal and mechanical properties of poly(ethylene-co-vinyl acetate) (EVA) with differents organophilic bentonites, which were chemically modified with ammonium salt and with an ammonium salt-free agent.

## Materials

The following materials were used for the preparation of the EVA/bentonite samples (1.5 and 3.0 wt %): EVA 3019 PE supplied by Braskem with an 18 wt % vinyl acetate content; the sodium bentonite Vulgel CN 45 supplied by Aliança Latina Indústria e Comércio Ltda; and the ammonium salt-free organophilic bentonite Novaclay™ was supplied by Ioto International and designated as BN and BN-AM, respectively. The sodium bentonite Cloisite®, which was supplied by Southern Clay Products, and the one modified with ammonium salt-free surfactant, using the AM suffix, therefore being denominated BI and BI-AM, respectively. The CT suffix was used to designate the organophilic bentonites modified with the ammonium surfactant, cetyltrimethylammonium bromide salt of the Vetec Química Fina brand. The ammonium salt-free surfactant (AM) used, which was supplied by Ioto International, is a surface-modifying agent containing 18 carbon atoms in its chemical structure.

## Methods

The 1.5% and 3.0 wt % of EVA/bentonite was previously mixed in an intensive homogenizer, of the MH Equipments brand, model MH 50H, at 3,600 rpm and processed in a single-screw laboratory extruder with a 25 mm diameter (D) and a 32 L/D ratio (130 °C at 200 rpm). The obtained strands were pelletized and these were submitted to the injection process using a ROMI injector model PRIMAX 65R, with a mould for tensile specimens. The injection pressure was 300 bar, the pressure and hold time were 150 bar and 2 seconds, respectively.

The surface of the materials ($170 \times 20 \times 3$ mmm) was evaluated using a Tecnival optical microscope model SQF with a 4X Zoom. The materials were evaluated using differential scanning calorimetry (DSC) technique in a Netzsch equipment model 200 F3 Maia, submitted to the following temperature conditions: heating and cooling rate of 10 °C $\text{min}^{-1}$, from −70 °C to 200 °C, from 200 °C to −70 °C; the thermogravimetric analysis (TGA) in the Netzsch Model TG 209 equipment submitted to a 20 to 860 °C, with a heating ratio of 200 °C $\text{min}^{-1}$ and the following atmosphere programming: 1) 20 to 560 °C – nitrogen; and 2) 560 to 860 °C – oxygen.

Tensile tests were performed using a universal test machine Instron 5567 model at a crosshead speed of 500 $\text{mm.min}^{-1}$ at room temperature, according to the ASTM D 638.

## Results and Discussion

Figure 1 shows the images and their expansions of the specimens of injected materials. Besides the difference in color of the nanocomposites some materials containing non-modified bentonite had small dark region, indicating the formation of small agglomerates of bentonite clay within the polymer matrix. The cluster formation was influenced by the ability to comply phases, in general, nanocomposites containing organoclay showed a better behavior to natural clays.

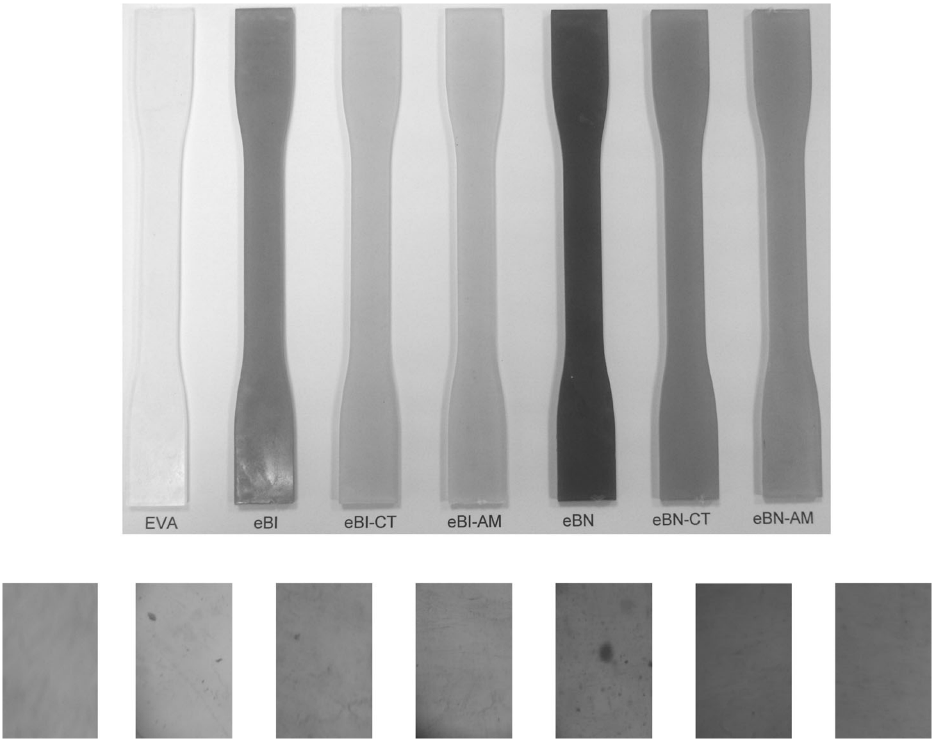

**Figure 1.**
Image and microscopy expansion for EVA and EVA/bentonites samples with 3.0 wt %.

The values obtained by DSC for the materials containing sodium bentonite (BN) the modified ones (CT and AM) are presented in Table 1.

In comparison to the EVA polymer, the addition of sodium bentonite (BN) did not change the crystalline melting temperature ($T_m$) and crystallization temperature ($T_c$) of the materials. However, the addition of 1.5 wt % significantly decreased the glass transition temperature ($T_g$), a behavior that was not noticed in the compositions with greater concentrations of bentonite. This factor might be associated to the effect of the interaction between the bentonite and the matrix, in which the increase in the inorganic fillers content limits the movements of the segments in the polymer chain due to the electrostatic interaction with the filler.[15] Similarly, the nanocomposites containing modified bentonites (eBN-CT and eBN-AM) presented the same behavior profile within the evaluated parameters and only at $T_m$ these materials presented a slight increase in temperature.

The presence of modifiers contained in the bentonite influenced the thermal behavior of the nanocomposites, especially in the crystalline fusion enthalpy ($\Delta H_m$). Both with CT and with AM this property increased significantly, which proves a better interaction of the polymer with the added filler in relation to the non-modified bentonite, which is expected for polymer nanocomposites. The presence of modifiers on the MMT surface, especially the clay mineral present in bentonites, allowed compatibility among stages, making the material more homogeneous, and therefore contributing to the changes in thermal properties.

The effect of the presence of these materials in the polymer was clearly observed in the increase of crystallinity, because the structure of the clay minerals dispersed in the polymer/clay nanocomposites always acts as an agent of heterogeneous nucleation for spherulites, due to the decrease in size of the latter.[16] Even though the nucleating effect of the clay minerals is more evident in low concentrations, of up to 5 wt %, for the increase might difficult the movement of the polymer chains delaying the crystallization of spherulites, the clay minerals might perform two functions in the crystallization, one as nucleating agent facilitating the crystallization process and other as a physical obstacle to delay crystallization.[17]

The DSC results referring to sodium bentonite BI and modified (CT and AM) are presented in Table 2.

The nanocomposite containing 1.5 wt % of the BI bentonite presented an increase in the $T_g$ value in comparison with the that of the EVA. This behavior must have had direct influence on the amorphous phase of the polymer, making it more susceptible to the thermal effect in which the movement of the polymer chains was blocked by the presence of the clay mineral. Still, the interaction between of the inorganic material and the matrix was more effective, therefore inhibiting the movement of segments from the polymer chain.

The main contributions by the presence of modified bentonites were $\Delta H_m$ and

**Table 1.**
Thermal parameters for EVA and EVA/BN nanocomposites obtained by differential scanning calorimetry (DSC).

| Sample | wt % | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J.g$^{-1}$) | $T_c$ (°C) | $\chi$ (%)* |
|---|---|---|---|---|---|---|
| EVA | | −35.0 | 84.6 | 66.6 | 65.0 | 22.7 |
| eBN | 1.5 | −46.6 | 85.6 | 72.9 | 66.3 | 24.9 |
| | 3.0 | −33.5 | 84.6 | 67.2 | 66.0 | 22.9 |
| eBN-CT | 1.5 | −49.0 | 86.1 | 70.5 | 63.8 | 24.0 |
| | 3.0 | −44.7 | 86.2 | 80.6 | 65.1 | 27.5 |
| eBN-AM | 1.5 | −21.0 | 88.2 | 78.3 | 63.7 | 26.7 |
| | 3.0 | −26.0 | 85.8 | 81.6 | 64.8 | 27.8 |

* $\chi = \Delta H_m / \Delta H^\circ_m . 100$; $\Delta H^\circ_m$(PE 100% crystalline) = 293 J.g$^{-1}$.

**Table 2.**
Thermal parameters for EVA and EVA/BN nanocomposites obtained by differential scanning calorimetry (DSC).

| Sample | wt % | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J.g$^{-1}$) | $T_c$ (°C) | χ (%)* |
|---|---|---|---|---|---|---|
| EVA | | −35.0 | 84.6 | 66.6 | 65.0 | 22.7 |
| eBI | 1.5 | −24.9 | 83.5 | 67.6 | 64.2 | 23.1 |
| | 3.0 | −41.8 | 85.3 | 63.6 | 63.9 | 21.7 |
| eBI-CT | 1.5 | −42.7 | 85.8 | 74.7 | 66.3 | 25.5 |
| | 3.0 | −26.6 | 82.3 | 70.2 | 63.8 | 23.9 |
| eBI-AM | 1.5 | −26.4 | 85.4 | 75.3 | 65.2 | 25.7 |
| | 3.0 | −28.1 | 88.7 | 73.3 | 63.9 | 25.0 |

$^{*}\chi = \Delta H_m / \Delta H^{\circ}_m . 100$; $\Delta H^{\circ}_m$(PE 100% crystalline) = 293 J.g$^{-1}$.

crystallinity. Similarly to the results previously discussed, the increase in the amount of filler in the polymer increases crystallinity, showing once again the favored nucleating effect. In a certain way, it is known the entire process, both of extrusion and injection, is influenced by the heating or cooling rate, therefore, it interferes in the crystallization behavior. In the case of industries, an increase in it leads to a decrease in the time of the cycle of production of parts, for it prevents them from shrinking and makes the process faster and more productive.[18]

The thermogravimetry curves (Figures 2 and 3) of all materials presented the same degradation profile in two stages of loss of mass. The presence of different modifiers bentonites in the EVA decreased the initial temperature of the degradation process $T_{onset}$ in the first stage of loss of mass, being mainly eBN, which contains unmodified sodium bentonite. According to Zanetti (2001), the degradation process is probably accelerated due to the acid catalysis promoted by the presence of protonated MMT.[19,20]

The effect of the modified bentonites content on the materials could be verified in the increase of the $T_{onset}$ value (Tables 3 and 4), mainly among the eBN-AM and eBI-AM compositions. This relative increase in thermal stability might be associated to better dispersion and interaction of the fillers with the polymer, since the presence of the modifier in the bentonite influences the compatibility between the materials.

The temperatures with maximum loss of mass (T), in the second stage in relation to the nanocomposites degradation processes, on their turn, had a decrease in value, a fact that might be associated to decreased

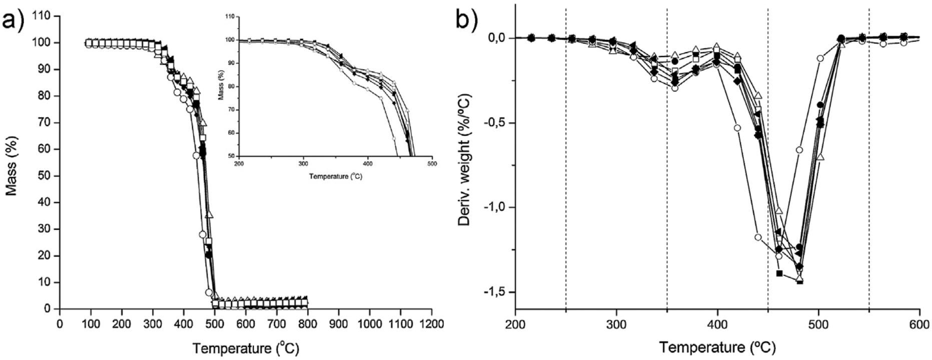

**Figure 2.**
TGA curves and expansion (a) and derivative thermogravimetric curves (DTG) (b) for EVA and EVA/BN bentonites, 1.5 and 3.0 wt % loadings; ■ = EVA, ● = eBN 1.5, Δ = eBN 3.0, ○ = eBN-CT 1.5, ◆ = eBN-CT 3.0, ◀ = eBN-AM 1.5, □ = eBN-AM 3.0.

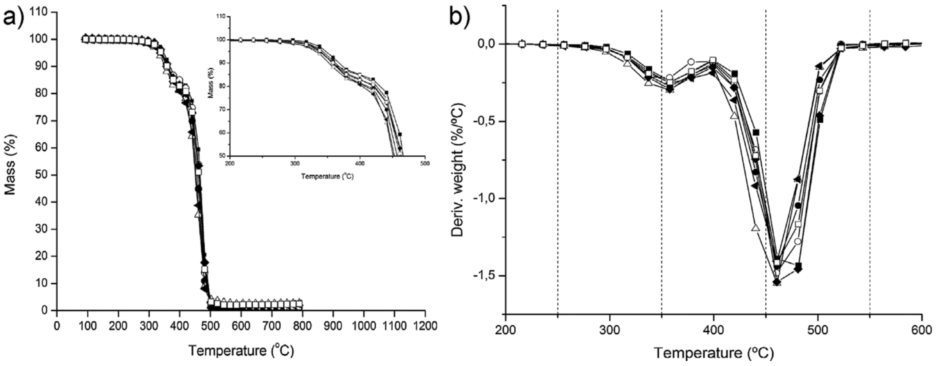

***Figure 3.***
TGA curves and expansion (a) and derivative thermogravimetric curves (DTG) (b) for EVA and EVA/BI bentonites, 1.5 and 3.0 wt % loadings; ■ = EVA, ● = eBI 1.5, Δ = eBI 3.0, ○ = eBI-CT 1.5, ◆ = eBI-CT 3.0, ◀ = eBI-AM 1.5, □ = eBI-AM 3.0.

***Table 3.***
TGA results of EVA and EVA/BN nanocomposites.

| SAMPLES | 1st degradation step | | | | 2nd degradation step | | | |
|---|---|---|---|---|---|---|---|---|
| | $T_{onset}$ | T | $T_{endset}$ | loss | $T_{onset}$ | T | $T_{endset}$ | loss |
| | | (°C) | | (%) | | (°C) | | (%) |
| EVA | 276.9 | 357.3 | 398.7 | 14.5 | 398.7 | 481.0 | 523.6 | 84.9 |
| eBN 1.5 | 217.6 | 298.0 | 348.5 | 14.8 | 399.7 | 473.1 | 524.0 | 82.5 |
| eBN 3.0 | 232.0 | 331.0 | 398.7 | 13.1 | 398.7 | 481.8 | 542.7 | 83.9 |
| eBN-CT 1.5 | 225.6 | 319.1 | 358.1 | 20.3 | 398.7 | 457.6 | 524.0 | 79.4 |
| eBN-CT 3.0 | 293.6 | 357.3 | 399.9 | 15.1 | 399.8 | 481.4 | 544.3 | 82.3 |
| eBN-AM 1.5 | 233.9 | 332.2 | 352.9 | 15.7 | 352.9 | 475.9 | 524.4 | 80.5 |
| eBN-AM 3.0 | 296.8 | 357.3 | 398.7 | 12.9 | 398.7 | 481.4 | 547.5 | 84.6 |

***Table 4.***
TGA results of EVA and EVA/BI nanocomposites.

| SAMPLES | 1st degradation step | | | | 2nd degradation step | | | |
|---|---|---|---|---|---|---|---|---|
| | $T_{onset}$ | T | $T_{endset}$ | loss | $T_{onset}$ | T | $T_{endset}$ | loss |
| | | (°C) | | (%) | | (°C) | | (%) |
| EVA | 276.9 | 357.3 | 398.7 | 14.5 | 398.7 | 481.0 | 523.6 | 84.9 |
| eBI 1.5 | 215.2 | 325.5 | 359.3 | 18.8 | 401.5 | 462.3 | 525.2 | 80.1 |
| eBI 3.0 | 207.3 | 321.5 | 354.1 | 16.5 | 399.9 | 460.7 | 522.0 | 81.2 |
| eBI-CT 1.5 | 239.9 | 321.5 | 349.3 | 14.5 | 399.5 | 461.9 | 524.0 | 83.9 |
| eBI-CT 3.0 | 237.9 | 321.1 | 348.1 | 14.5 | 398.7 | 459.5 | 522.0 | 85.5 |
| eBI-AM 1.5 | 279.2 | 325.9 | 358.5 | 19.3 | 399.5 | 461.5 | 523.6 | 78.0 |
| eBI-AM 3.0 | 287.7 | 324.7 | 355.7 | 14.9 | 398.3 | 460.3 | 518.4 | 83.0 |

interaction between polymer/filler, causing a greater availability of polymer chains to the thermal degradation process.

In the results of the mechanical behavior of tensile of the nanocomposites containing BI bentonites and modified ones, the influence of the natural bentonite modification was observed, through the increase in the elastic modulus and in the elongation (Figures 4a, b e c). A good dispersion of the MMT layered in general produces a greater increase in the elastic modulus and in the

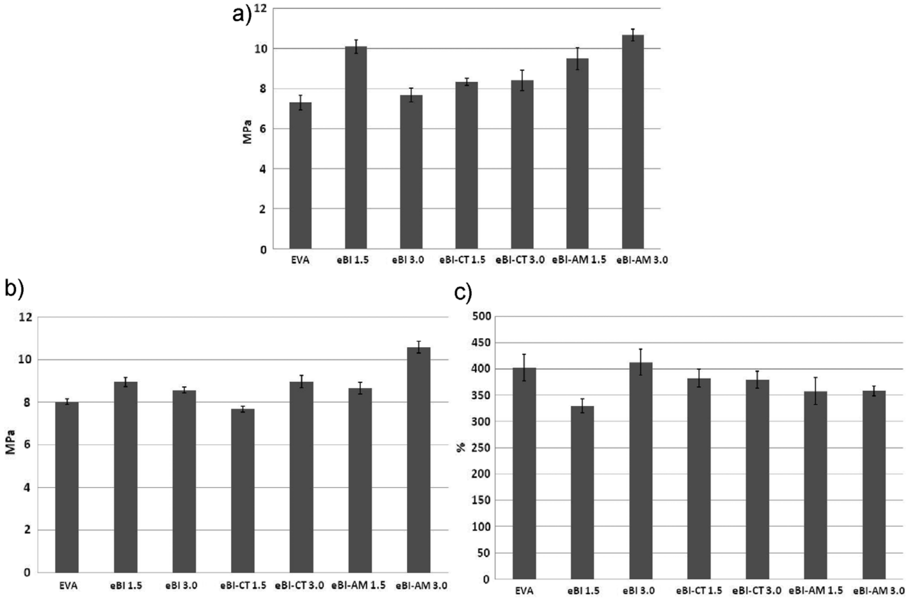

***Figure 4.***
(a) Elastic modulus, (b) Stress at break and (c) Elongation for EVA/BI nanocomposites.

tensile resistance, however, a significant decrease in ductility of the material.[21,22]

The elongation did not present significant improvement in relation to EVA, and the eBN 1.5 composition decreased the value of this parameter (Figures 5a, b e c). The loading effect of the modified bentonites on the EVA/BN nanocomposites was

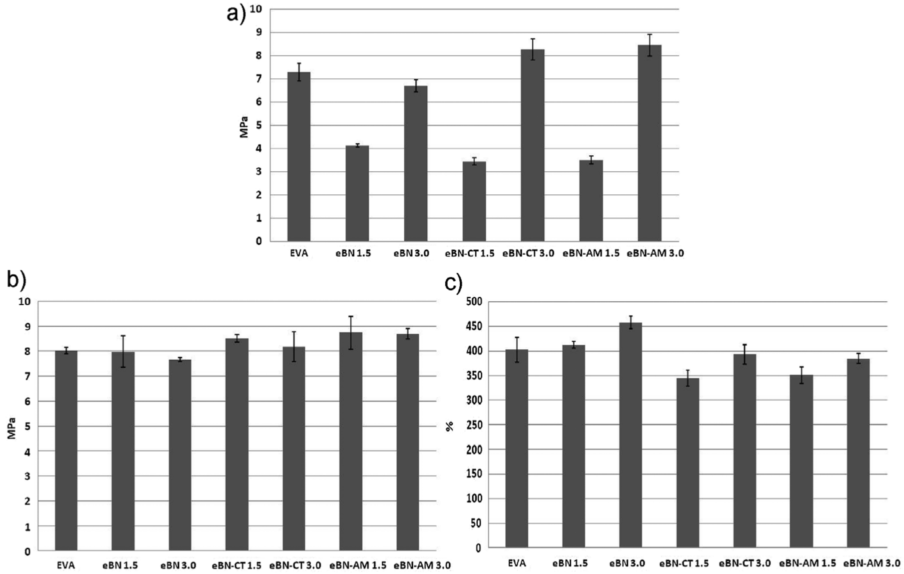

***Figure 5.***
(a) Elastic modulus for EVA/BN nanocomposites, (b) Stress at break and (c) Elongation for EVA/BN nanocomposites.

perceptible in the value of elastic modulus, in which greater values were presented by the greatest content of the filler and, on the other hand, the elongation was greater for these compositions. The values of the stress rupture did not present significant differences to define an individual behavior for each type of modified bentonite.

The eBN 3.0 nanocomposite, in particular, presented an interesting behavior in relation to the others, because the values of elastic modulus and strain, which were closer to those of the EVA, did not present loss in the mechanical property, which was justified by increased elongation. However, according to its TGA results, this composition presented lower thermal stability.

## Conclusion

The preparation and the characterization of bentonites were possible using two different modifiers in order to prepare EVA nanocomposites. The effect on different surfactants did not present significant changes in relation to the thermal and mechanical behavior of the EVA nanocomposites. However, bentonites containing both modifiers had a better compatibility performance with the polymer matrix in comparison to sodium bentonite. Finally, the proposal of using and investigating bentonite containing ammonium salt-free modifiers appears to be promising for other studies due to some limitations presented by quaternary ammonium salts.

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