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Evaluation of Impact Strength of Polyamide 6/Bentonite Clay Nanocomposites

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Nanocomposites of polymer/clay have had much attention in recent years, particularly those developed with layered silicates due to the need of engineering materials more efficient than pure polymers for certain applications. The level of exfoliation of layered silicates in crystalline structure of polymer matrices has been studied and has been observed that it affects the crystalline behavior and the physical and mechanical properties. In this study, nanocomposites of polyamide 6 were obtained by the melt intercalation method, using a Brazilian bentonite modified with a quaternary ammonium salt. X-Ray Diffraction (XRD) results showed the incorporation of salt among the layers of clay, making it organophilic and that the nanocomposites presented exfoliated and/or partially exfoliated structures and confirmed by transmission electron microscopy (TEM). By thermogravimetry (TG), the results indicated that the presence of clay increased the thermal stability of polyamide 6. The impact properties of the nanocomposites showed inferior values in relation to the pure polyamide, in other words, decrease the toughness.

Keywords: *nanocomposites, organoclay, polyamide 6*

1. Introduction

In recent years there has been much attention given to polymer-clay nanocomposites, particularly those developed with layered silicates due to the need of more efficient engineering materials, and because of the fact that pure polymers do not present the properties needed for certain applications. Several methods have been applied for the preparation of polymer-clay nanocomposites, such as melting intercalation, the most used among them[1].

Polymeric nanocomposites are hybrid materials where inorganic nanosized substances are dispersed in a polymer matrix[2-3]. Polymer layered silicate nanocomposites are compared to conventional polymeric composites due to the use of fillers to improve some specific properties[1]. Such nanocomposites present improvement on mechanical, thermal, flammability and dimensional stability properties, using low concentrations of silicate, around 1-5% by weight[4].

From the surveys conducted by the Toyota group which developed polyamide 6 nanocomposites using small amounts of montmorillonite clay and obtained a significant increase in mechanical and thermal properties, several other studies have been conducted in order to achieve synergy among the parts[5,6-12].

Layered silicates which are used as fillers present particles with nanometric dimensions (100-500 nm) and have a high surface area which promotes better interaction with the polymer matrix and therefore an improvement in physical properties[5]. Several polymers have been used in the preparation of polymer-clay nanocomposites, such as polystyrene, polyamide 6 and 66, polycarbonate, polyolefins, etc[13]. The effect of the presence of layered silicates and the level of exfoliation of the crystalline structure of polymer matrices have been studied and it has been observed that they affect crystalline behavior and hence physical and mechanical properties[14]. The objective of this work was to analyze the effect of the Brazilian clay incorporation on the mechanical strength under the impact of polyamide 6/bentonite clay nanocomposites.

2. Materials and Methods

2.1. *Materials*

Bentonite clay Brasgel PA (sodium), with CEC (cation exchange capacity) = 90 mEq/100 (method of adsorption of methylene blue) passed through ABNT sieve no. 200 (D = 74 µm), cream colored, supplied by Bentonit União Nordeste (BUN) located in Campina Grande-PB. The clay was called untreated clay (MMT) because montmorillonite is the predominant clay mineral.

The polymer matrix used was a polyamide 6 (Technyl C216) provided by Rhodia/ SP, in the form of white pelets.

We used the quaternary ammonium salt Cetremide (hexadecyltrimethyl ammonium bromide), produced by Vetec/SP.

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2.2. *Methods*

To make clay compatible with the polymer matrix, the sodium ions present between the layers of clay were exchanged for ions of the quaternary ammonium salt (Cetremide) to produce the organoclay, called OMMT. This exchange was performed in the presence of the quaternary ammonium salt Cetremide. To obtain organoclay (OMMT) a suitable treatment was conducted for the salt, based on the CEC of clay, according to procedure reported in previous studies[2,4,14].

Before any processing step, all materials containing polyamide were dried at 80 °C for 24 hours in the vacuum oven.

To obtain nanocomposites we used a preparation of a concentrate of polyamide and clay (1:1) in an internal mixer coupled to a Torque Rheometer System 90 by Haake-Büchler, operating at 240 °C, 60 rpm for 10 minutes. The concentrate obtained was crushed in a grinder of knives and then added to the polymer matrix in quantities necessary to obtain nominal concentrations of 3 wt (%) clay.

The mixture polyamide 6/organoclay was processed in a corrotational Werner-Pfleiderer ZSK 30 twin screw extruder at a temperature of 220 °C on the 1st zone and 240 °C on the other heating zones. We used two rotational speeds of the threads 100 and 200 rpm, feed rates of 5 and 10 kg/h and two screw profiles R1 and R2.

The threads are composed of various transport elements, but the difference between them is in the mixing zone. For comparison, pure polyamide 6 was extruded under the same mixing conditions, at a feed rate of 5 kg/h.

Samples were named as 5100R1, which means, feeding rate of 5 kg/h speed of 100 rpm and R1 screw. The other samples follow the same naming pattern. The changes in rotational speed, thread profile and feed rate were conducted to evaluate the effect of these processing variables on the structure and mechanical behavior of the polyamide 6 nanocomposites obtained.

After extrusion, the material was granulated and dried at 80 °C in the vacuum oven for 24 hours, and processed by injection moulding in an Arbug Allrounder 270/30 t machine. The specimens were prepared for tensile and impact testings according to the ASTM D638, D256, respectively.

The clay and the nanocomposites were characterized by X-ray diffraction (XRD). Moreover, the nanocomposites were also characterized by transmission electron microscopy (TEM), thermogravimetry (TG) and mechanical properties.

3. Results and Discussion

3.1. *X-RAY Diffraction (XRD)*

To evaluate the formation of polyamide 6/organoclay nanocomposites, the systems were characterized by XRD. Figure 1 shows the XRD diffraction patterns for polyamide 6 (PA6) and the PA6/organoclay (OMMT) systems. The XRD curve for OMMT clay is also shown for comparison. It is noticed that the peak of the organoclay with d_{001} = 21.34 Å disappeared when it was incorporated into the polyamide 6 matrix and apparently a small shoulder appeared for all nanocomposites around 6.2 degrees. These results may indicate that all systems showed exfoliated and/or partially exfoliated structures, similar results were found in the literature[5,10,11]. It is interesting to notice that the nanocomposites patterns presented the same behavior regardless the processing variables used. These results are consistent with other works reported in the literature[15,16].

3.2. *Transmission Electron Microscopy (TEM)*

The transmission electron microscopy was used to analyze the morphology of the nanocomposites and to confirm the X-ray diffraction results. Figure 2 shows

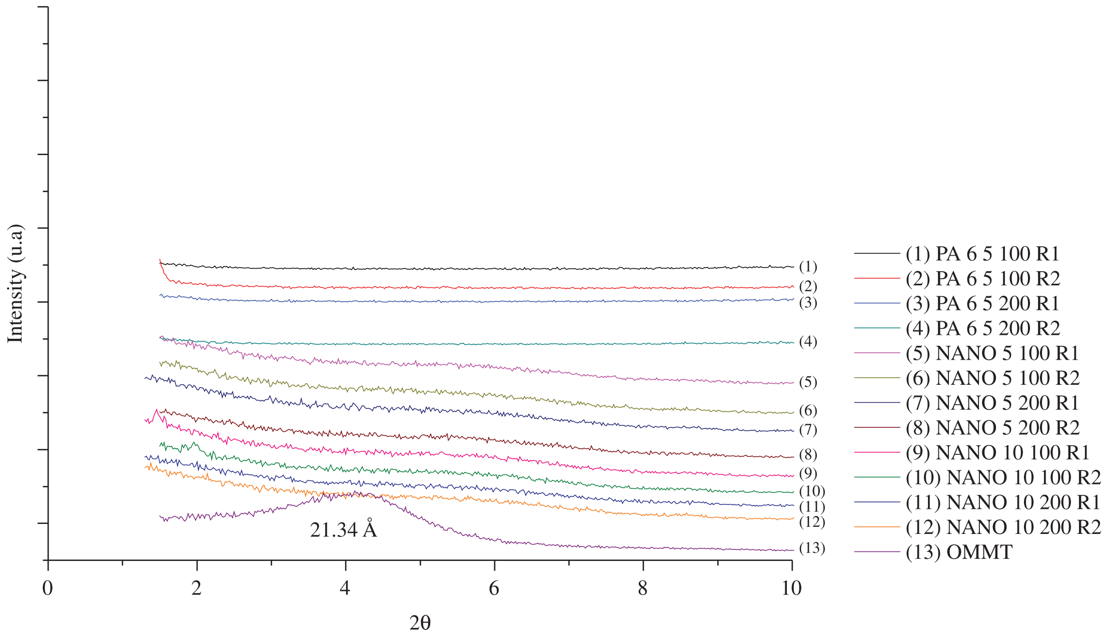


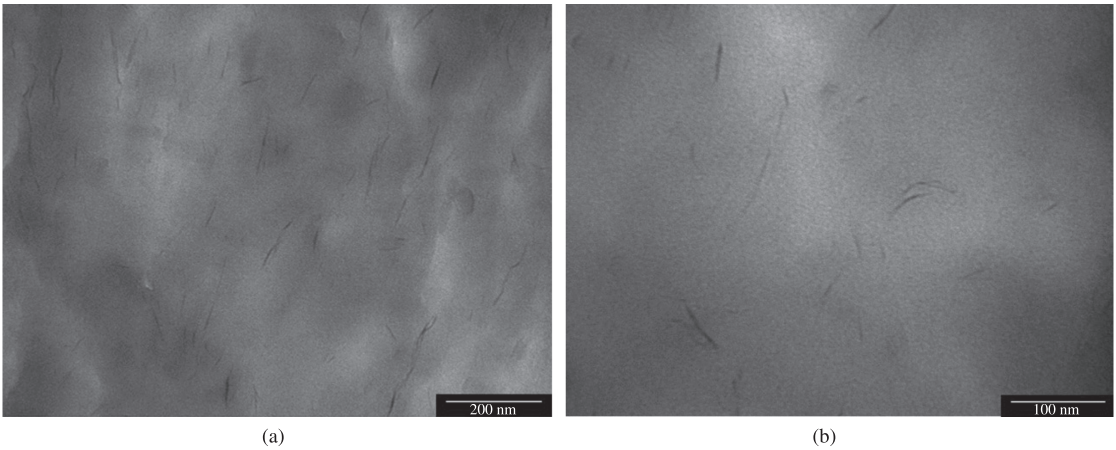
Figure 1. XRD patterns of organoclay, polyamide 6 and PA6/organoclay systems.

representative images obtained for all compositions. They present morphologies composed of exfoliated clay lamellae and well distributed in the polymer matrix. Similar results were observed in the literature[5,10,16] with nanocomposites obtained from commercial clays These images corroborate the results of X-ray diffraction.

As expected, the presence of the salt on the surface of the clay can change from hydrophilic to hydrophobic characteristic improving the wettability between PA6 and organoclay and promoting the exfoliation of clays in the PA6 matrix.

3.3. *Thermogravimetry (TG)*

TG curves of PA6 and its nanocomposites are shown in Figure 3. An important feature to note is that all samples present the decomposition steps. It can be observed that the clay almost not changed the degradation temperature of the pure polymer. Close to 200 °C appears an event that may be associated with the decomposition of organic salt and some moisture. Above 400 °C begins to appear decomposition or other events of mass loss that may be related the polymer matrix. These results indicate that the presence of clay maintained the thermal stability of polyamide 6.



(a) (b)

Figure 2. TEM photomicrographs of PA6/organoclay nanocomposites.

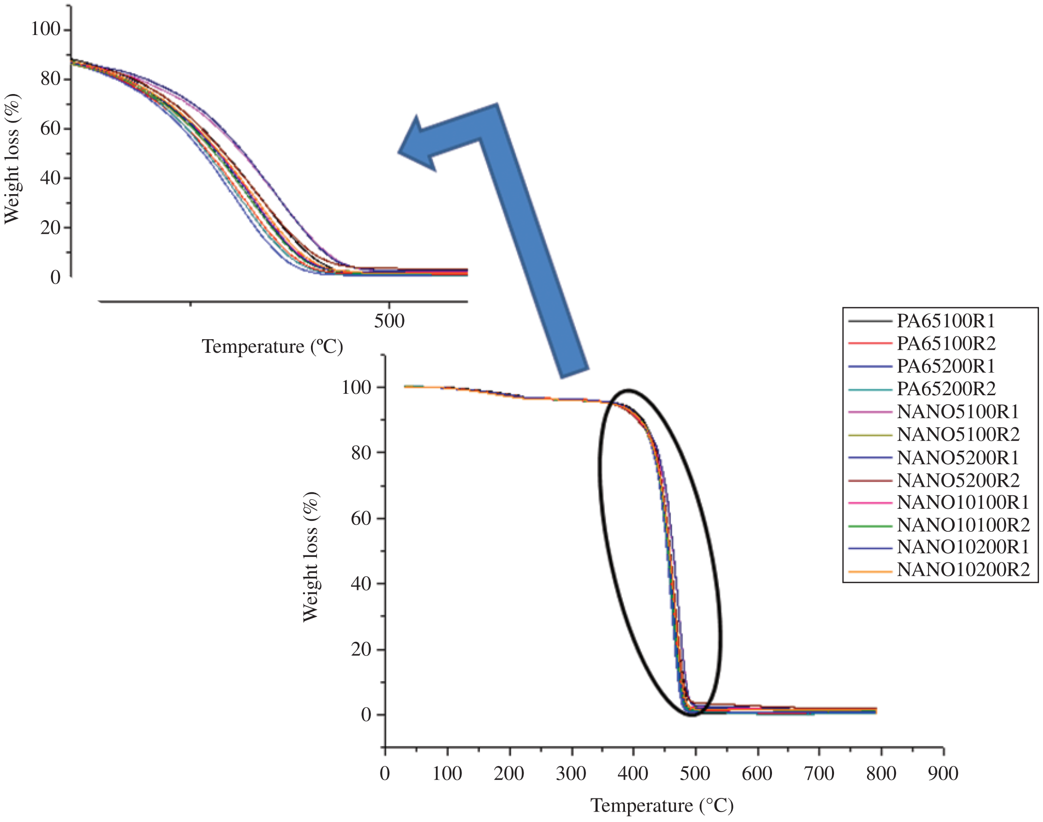


Figure 3. TG curves of polyamide 6 and its nanocomposites.

Table 1. Young modulus and impact strength of polyamide 6 and its nanocomposites.

Sample	Young modulus (GPa)	Izod impact strength ($J.m^{-1}$)
PA6 5 100 R1	2.9 ± 0.1	41.0 ± 4.5
PA6 5 100 R2	2.9 ± 0.2	47.0 ± 2.7
PA6 5 200 R1	3.3 ± 3.2	40.8 ± 3.2
PA6 5 200 R2	3.4 ± 0.3	44.3 ± 5.8
NANO 5 100 R1	3.5 ± 0.1	34.7 ± 4.1
NANO 5 100 R2	3.6 ± 0.1	39.4 ± 2.5
NANO 5 200 R1	3.5 ± 0.1	33.9 ± 2.7
NANO 5 200 R2	3.7 ± 0.0	35.5 ± 1.7
NANO 10 100 R1	3.5 ± 0.1	36.2 ± 3.1
NANO 10 100 R2	3.6 ± 0.0	35.7 ± 2.6
NANO 10 200 R1	3.6 ± 0.1	30.6 ± 2.7
NANO 10 200 R2	3.5 ± 0.1	35.4 ± 3.7

3.4. *Izod impact on mechanical testings*

According to Sinha Ray and Okamoto[5] and Alexandre and Dubois[13], the polymer-clay systems containing low clay content (<10%) present better mechanical properties compared to pure polyamide. This increase is due to stronger interfacial interaction between the matrix and the layers of clay.

Table 1 shows the elastic modulus and the impact strength of pure polyamide and its nanocomposites. It can be observed that nanocomposites showed a reduction of around 10% on average in impact strength, ie, loss of toughness, when compared to the pure polyamides. This can be attributed to the greater rigidity of these systems[8]. These results were also confirmed by an increase on the Young modulus and can be attributed to the occurrence of dispersion of silicate layers in polymer matrix and strong interactions of functional groups of PA6 with the clay surface, as reported in the literature[5].

4. Conclusions

Polyamide 6/organoclay nanocomposites were obtained with success by melt intercalation technique. By X-ray diffraction was possible to observe exfoliated and/or partially exfoliated structures. By transmission electron microscopy, all the nanocomposites exhibited morphologies exfoliated clay lamellae and well distributed in the polymer matrix. The results from thermogravimetry analysis indicated that the presence of clay almost not changed the thermal stability of polyamide 6, and mechanical characterization under impact showed that the nanocomposites presented inferior properties compared to pure polyamide, that is, loss of toughness. The results also indicated an increase on the Young modulus.

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