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PREPARATION AND CHARACTERIZATION OF PBT/CLAY NANOCOMPOSITE

Mariana N. Sartori[1], Rene R. Oliveira[1], Francisco R. V. Díaz[2], Angel Visentim Ortiz[1], Vijaya K. Rangari[3], Esperidiana A. B. Moura[1]*

[1]Nuclear and Energy Research Institute, IPEN-CNEN/SP
2242 Prof. L. Prestes Av., São Paulo, SP, 05508-000, Brazil
[2]Metallurgical and Materials Engineering Department,
Polytechnic School, University of São Paulo
2463 Av. Prof. Mello de Morais, São Paulo, SP, 05508-900, Brazil
[3] Tuskegee University
Department of Materials Science and Engineering
1200 W. Montgomery Rd., Tuskegee, AL, 36088, U.S.A.
*eabmoura@ipen.br

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Abstract

This work presents the preparation and characterization of a nanocomposite based on Poly(butylene terephthalate) PBT and Brazilian smectitic clay (bentonite chocolate clay). Before being incorporated as clay nanoparticles in PBT resin, the clay was organically modified by the addition of a quaternary salt and sodium carbonate. PBT/Clay nanocomposite (96.3:3.70 wt %) was obtained by using a twin-screw extruder machine. After extrusion process, the nanocomposite was characterized by tensile, flexural and impact tests, SEM, Vicat, HDT, DSC, TGA and XRD tests. The results showed that the properties of the nanocomposite obtained were superior to those of neat PBT. Concerning the temperature of thermal distortion (HDT) an expressive gain of around 45 % was presented to PBT/Clay nanocomposite compared to PBT evidencing the interaction of nanofiller with the polymeric matrix.

Introduction

Polymer-clay nanocomposites, also called as polymer layered silicates nanocomposites have attracted much attention from both industry and academia over the past decade because they frequently exhibit unexpected properties. In contrast to the traditional fillers, nanofillers, in particular, nanoclay, is found to be effective. The addition of a small amount (< 5 wt.%) can show significant improvement in mechanical, thermal and barrier properties, flammability resistance, and electrical/electronic properties of the final polymer nanocomposite without requiring special processing techniques. Also, as with other nano-size particles, the overall crystallization rate and the glass transition temperature are also affected. It is generally believed that the improvement of properties of nanoclay composites is directly related to the complete exfoliation of silicate layers in the polymer matrix. However, a processing technique that produces complete exfoliation is still a technical challenge [1, 2].

Polymer-clay nanocomposites comprised of a semicrystalline polymer matrix are particularly attractive because of the dramatic improvement in heat distortion temperature and modulus provided by the nanoparticle reinforcement and the crystallization behavior inherent to most commodity semicrystalline thermoplastics [3].

Poly(butylene terephthalate), a typical semicrystalline polymer, is an important commercially available engineering thermoplastic polyester for injection molding applications because of its excellent process ability and mechanical properties. PBT has been widely used in various applications such as an insulator in the electrical and electronic industries and engineering materials. It is widely used for connectors in personal computer industry because of its good combination of rigidity and solvent resistance. However, the disadvantages such as low impact strength, high brittleness, cost, and low heat distortion temperature limit the applications of PBT. Many attempts have been made to obtain desirable properties of PBT. Several studies have been widely reported in the scientific literature on the structure–property relationships of the PBT–clay nanocomposites [4-9].

Bentonite, a clay composed essentially of one or more of the smectite group clay minerals especially montmorillonite is the most commonly clay used in obtaining nanocomposite polymer/clay. However, bentonite clay should be organically modified with quaternary ammonium salts to improve their interaction with the polymer matrix. Therefore, this work presents the preparation and characterization of PBT/organoclay based on PBT and a natural Brazilian bentonite chocolate clay.

Experimental

Materials

The materials used in this study were PBT resin (Celanex 1600A- commercial grade by Ticona Engineering Polymers) with MFI = 16.72 g/10 min at 190 ^{0}C/2.16 Kg, specific density = 1.332 g/cm^3, and natural Brazilian bentonite chocolate clay from Boa-Vista, PB, Brazil.

Nanoclay preparation

Before the bentonite chocolate clay becomes ready to be incorporated as a nanoparticle in the composite, clay should be modified by quaternary ammonium compounds, for example, to make an intercalated nanocomposite exfoliate. In this work, the clay was modified by the addition of a quaternary salt and sodium carbonate and underwent the processes of dispersion into water, stirring and heating for a determinate time, and just then was it filtered and dried for the disaggregation of one particle in another, and finally characterized.

Nanocomposite preparation

PBT/Clay nanocomposite (70 % / 3 %, based on wt %), was obtained with an extrusion machine twin screw "extruder ZSK 18 Megalab" made by Coperion Werner & Pfleiderer GmbH & Co. KG. The compounded materials passed through the different zones of the extruder and were finally extruded. The extrudates coming out of the extruder were cooled down by using cold water for a better dimensional stability, and they were wound up manually. Finally, the PBT/Clay nanocomposite (70:30 wt %) was dried, pelletized by a pelletizer, fed into an injection molding machine and specimen test samples were obtained.

Analyses

X-rays diffraction (XRD): XRD is most commonly used to probe the nanocomposites structure and occasionally to study the kinetics of the polymer melt intercalation owing to its ease and availability [10]. XRD, in this study was used to evaluate the modification of bentonite chocolate clay and the intercalation in the PBT matrix. XRD patterns for the clay were recorded on a Simens - D5000 diffractometer operated at 40 kV and 40 mA, with CuKα radiation ($\lambda = 1.54$ nm). XRD for the PBT and PBT/Clay nanocomposite was carried out using a diffractometer Rigaku Denki Co. Ltd., Multiflex model with CuKα radiation ($\lambda = 1.5406$ Å) at 40 kV and 20 mA, with 2θ varying between 2° to 50°.

Mechanical and Thermo-mechanical tests: PBT/Clay nanocomposite was characterized by: tensile (ASTM D 638), flexural (ASTM D 790), heat distortion temperature (HDT) (ASTM D 648) and Vicat softening temperature (ASTM D 1525).

Differential Scanning Calorimetry (DSC): the DSC analyses of PBT and PBT/Clay nanocomposite samples were carried out using a SDT Q 600 (TA Instruments), on four weighed samples with 5.0 ± 0.5 mg of material. Samples were heated from 25 to 300 °C, at a heating rate of 10 °C/min (in an oxygen atmosphere). The scans were taken from the second heating cycle to eliminate any thermal history of the samples. Crystallinity was calculated from melting peak areas. The percentage of crystallinity (Xc) of nanocomposite material was calculated by the following equation:

$$Xc = \frac{\Delta Hm \cdot 100}{\Delta H^0 m \cdot w} \qquad (1)$$

where:

$\Delta H_m{}^*$ = melting enthalpy of the of PBT/Clay nanocomposite
$\Delta H^0{}_m$ = initial melting enthalpy of the PBT assuming 100 % crystallinity, 140 J/g
W = polymer mass fraction in the composite

Thermogravimetric Analyses (TG): the TG of PBT and PBT/Clay nanocomposite samples were carried out using a a SDT Q 600 (TA Instruments). TG analyses of the materials were performed on three weighed samples with 5.0 ± 0.5 mg of the materials. Samples were heated from 25 to 600 °C, at a heating rate of 10 °C/min (in an oxygen atmosphere).

Scanning Electron Microscopy (SEM): The scanning electron microscopy (SEM) analyses for samples of the PBT and PBT/Clay nanocomposite that were cryo-fractured under liquid nitrogen were carried out using a LX 30 (Philips) instrument. The fractured surface of samples was coated with a fine layer of gold and observed by scanning electron microscopy.

Statistical analysis: The differences between the results of tests carried out were statistically evaluated by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

Results and Discussion

Bentonite Chocolate Clay Characterization Results

X-ray diffraction (XRD): the XRD results of natural bentonite chocolate and after be modified by quaternary ammonium salt are showed in Figure1. The results show that the natural bentonite chocoloate presented an interlayer distance (d_{001}) of 14.7 Å and after modification the interlayer distance increased to 19Å. This increase confirms the intercalation of the quaternary ammonium cation in the interlamellar spacings of the chocolate clay took place.

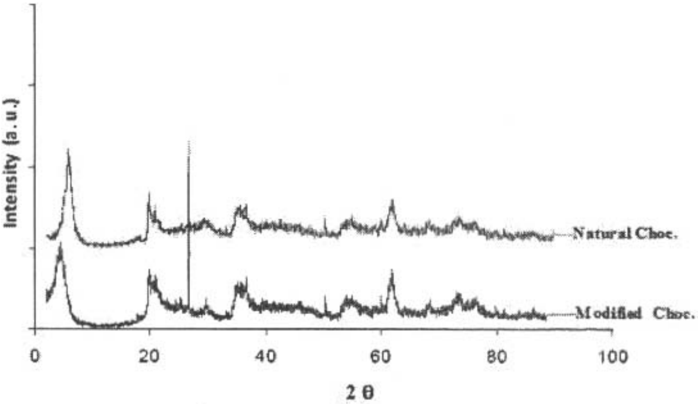

Figure 1. X-rays diffraction patterns of natural bentonite chocolate clay and after modification with quaternary ammonium salt.

PBT/Clay Nanocomposite Characterization

X-rays diffraction (XRD): Figure 2 shows the XRD pattern for the modified bentonite chocolate clay, PBT and PBT/Clay nanocomposite in the range of 2θ between 2° to 50°. The XRD pattern of PBT/Clay nanocomposite exhibits change at intensity and inclination of peak at around $2\theta = 21$. This indicates that PBT chains have diffused into the gallery of the clay and that the clay has been successfully intercalated in the PBT matrix.

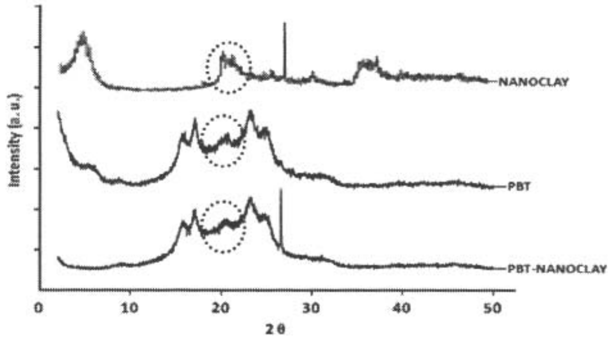

Figure 2. X-rays diffraction patterns of modified bentonite chocolate clay, PBT and PBT/Clay nanocomposite

Mechanical and Thermo-Mechanical Tests Results

These results of the mechanical and thermo-mechanical tests presented show the average values calculated from the data obtained in tests, with standard deviations less than 10 % for all tests.

Tensile tests: Figure 3 shows the results of the tensile strength at break and elongation at break (%) for both, PBT and PBT/Clay nanocomposite. An increase of around 60 % ($p < 0.05$) in tensile strength at break of neat PBT due to clay addition can be seen, whereas the elongation at break has drastically been reduced. These changes should be associated with the interfacial interaction between the PBT and bentonite chocolate clay.

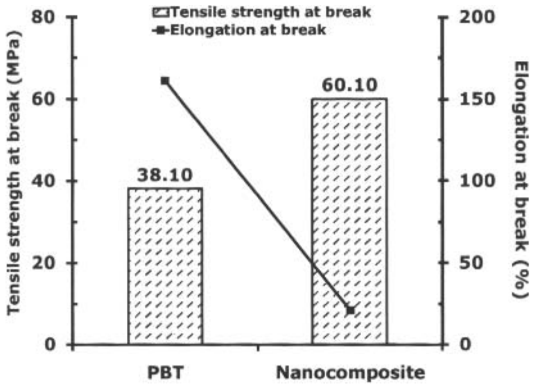

Figure 3. Tensile strength at break and elongation at break (%) for both, PBT and PBT/Clay nanocomposite.

Flexural tests: The flexural strength and modulus tests results for both, PBT and PBT/Clay nanocompostite are presented in Figure 4. It can be seen that the flexural strength of neat PBT increased ca. 25 % and the flexural modulus of around 15 % by the addition of bentonite chocolate clay. These are due to the intercalation and reinforcing effects of clay.

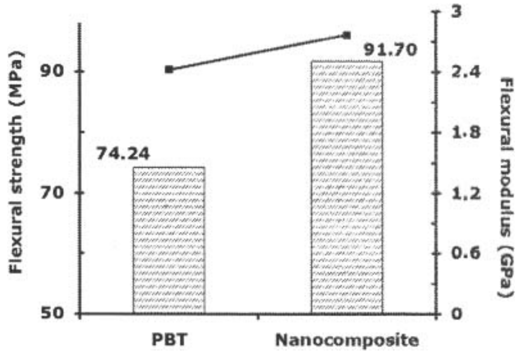

Figure 4. The flexural strength, for PBT and PBT/Clay nanocomposite

HDT and Vicat tests: In Figure 5, HDT and Vicat testing results, for both, PBT and PBT/Clay nanocomposite are shown. As it can be seen bentonite chocolate clay addition in PBT provided an important gain in HDT of about 45 % and a slight tendency for an increase in Vicat softening temperature.

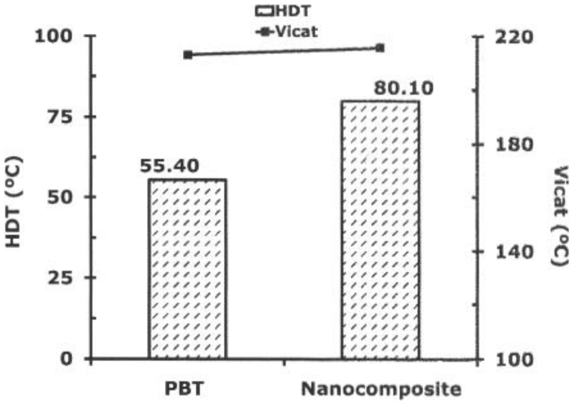

Figure 5. HDT and Vicat, for PBT and PBT/Clay nanocomposite.

Differential Scanning Calorimetry (DSC)

The results of the DSC analysis for melting enthalpy, melting temperature, and crystallinity percentage for the PBT and PBT/Clay nanocomposite are given in Table I. As it can be seen, the melting enthalpy values of neat PBT increased, about 10 %, and the crystallinity percentage of neat PBT increased from 29.22 % to 34.25 %, due to the bentonite chocolate clay addition. This is attributed to the nucleation effects of clay and the improvement in the crystal perfection of PBT. A similar observation is reported by Chow, S. W. for the PBT/Montmorillonite [10].

Thermogravimetric Analyses (TG)

The results of the thermogravimetric analyses (TG) are also presented in Table I. The results showed that there were no significant changes ($p < 0.05$) in the onset degradation temperature of PBT/Clay nanocomposite, when compared with those of neat PBT, but the total weight loss was about 7 % smaller than neat PBT.

Table I. Melting enthalpy, melting temperature, crystallinity (%), onset degradation temperature and total weight loss for the PBT and PBT/Clay nanocomposite

Materials	**ΔH_m[a] (J/g)**	**Xc[b] (%)**	**T_m[c] (°C)**	**Onset Temp[d] (°C)**	**Total Weight Loss[e] (%)**
PBT	41.01	29.22	212.87	332.49	89.62
PBT/Clay Nanocomposite	45.55	34.25	213.74	331.17	83.63

a. melting enthalpy; **b.** crystallinity percentage; **c.** melting temperature; **d.** onset degradation temperature; **e.** total weight loss.

Scanning Electron Microscopy (SEM)

SEM micrographs of cryo-fractured surfaces of PBT and PBT/Clay nanocomposite are shown in Figure 6. As it can be seen, PBT/Clay nanocomposite, Figure (6c) and Figure (6d), showed a slightly rough cryo-fractured surface, when compared with cryo-fractured surface of neat PBT (Figure 6a; Figure (6b). However, from Figure (6c) and Figure (6d), it can be revealed that some small particles dispersed in the PBT matrix. This suggests that some of the bentonite chocolate clay particles remain unexfoliated.

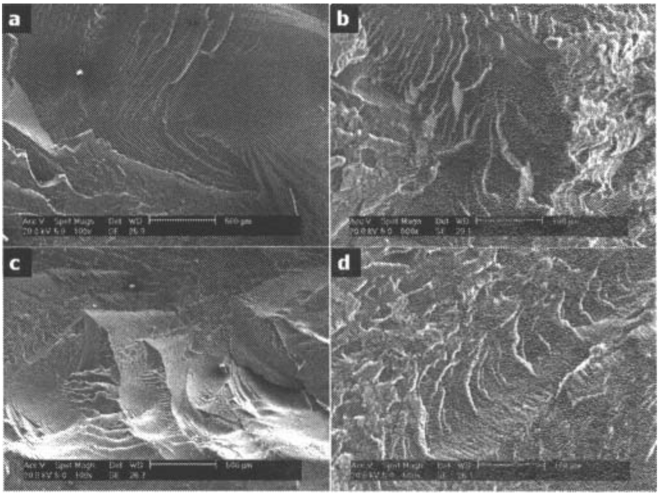

Figure 6. SEM micrographs for cryo-fractured surfaces of the PBT (6a) = 100 X; (6b) = 500 X and PBT/Clay nanocomposite (6c) =100 X; (6d) =500 X)

Conclusions

The objective of the present study was to evaluate the contribution of the natural Brazilian bentonite chocolate clay on properties of PBT. The PBT with bentonite chocolate clay was prepared using a twin-screw extruder and its properties were investigated. The results showed that the incorporation of nanoclay represented a significant gain in tensile strength at break, flexural strength, flexural modules, heat distortion temperature (HDT) and of crystallinity of PBT. The superior thermo-mechanical properties of PBT/Clay nanocomposite observed in this study can be attributed to the stiffness of Brazilian bentonite chocolate clay, reinforcing effects, to the degree of the intercalation and good dispersion of the clay layers in the PBT matrix, and increment of crystallinity for PBT.

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