2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-04-5**

STUDIES ON THERMO-MECHANICAL PROPERTIES OF PBT/CLAY NANOCOMPOSITE TREATED BY ELECTRON-BEAM RADIATION

Mariana N. Sartori [1a], Beatriz R. Nogueira[1b], Francisco R. V. Díaz[2] and Esperidiana A. B. Moura[1c]

[1]Nuclear and Energy Research Institute, IPEN-CNEN/SP
Av. Prof. L. Prestes 2242
05508-000 São Paulo, SP, Brazil
[a]mariana.sartori@hotmail.com
[b]bia.ribnog@gmail.com
[c]eabmoura@ipen.br

[2] Metallurgical and Materials Engineering Department
Polytechnic School,
University of São Paulo, Brazil

ABSTRACT

This work presents the study of electron-beam radiation effects on thermo-mechanical properties of PBT/Clay nanocomposite. Before being incorporated as clay nanoparticles in PBT resin, Brazilian smectitic clay (bentonite chocolate clay) was organically modified by the addition of a quaternary salt and sodium carbonate. The PBT resin and PBT/Clay nanocomposite (Nanocomposite) samples were irradiated at 70 kGy using a 1.5 MeV electron beam accelerator, at room temperature, in presence of air. The thermo-mechanical properties of irradiated and non-irradiated PBT and Nanocomposite, such as tensile strength, tensile modulus, elongation at break, HDT and Vicat were studied. The melt flow index (MFI) tests were also carried out and the correlation between their properties was discussed.

Keywords: PBT/nanoclay, bentonite chocolate clay, nanocomposite, thermo-mechanical properties, electron-beam radiation

1. INTRODUCTION

The term "nanocomposite" describes a two-phase material in which one of the phases is dispersed in the second one on a nanometer (10^{-9}m) level. This term is commonly used in two distinct areas of materials science: ceramics and polymers. However, we will only consider nanocomposites based on polymers. Nanocomposites are commonly based on polymer matrices reinforced by nanofillers such as precipitated silica, silica beads and cellulose whiskers, as well as colloidal dispersion of rigid polymers and many others [1, 2].

Polymer-clay interactions have been actively studied during the sixties and the early seventies but it is only recently that researchers from Toyota discovered the possibility to build a nanostructure from a polymer and an organophilic clay. Their new material based on polyamide 6 and organophilic montmorillonite, at low clay content (4 %, based on wt %) showed dramatic improvements of mechanical properties, barrier properties and thermal resistance when compared with the pristine matrix. Ever since, studies have shown that the use of clay in polymeric nanocomposites contribute to remarkable improvement in materials when compared with virgin polymers or conventional micro and macro composites. Recently, much effort has been made to develop polymer-clay nanocomposites and to understand the enhancement in properties upon addition and dispersion of organoclay in polymers [3 - 4].

Polybutylene terephthalate (PBT) is a thermoplastic engineering polymer, that is used as an insulator in the electrical and electronics industries. It is a thermoplastic (semi-) crystalline polymer and a type of polyester. PBT is resistant to solvents, shrinks very little during forming, is mechanically strong, has a heat-resistant of up to 150°C (or 200°C with glass-fibre reinforcement) and can be treated with flame retardants to make it noncombustible [5].

Nowadays, electron beam radiation has been efficiently applied for controllable modification in polymers. In general, electron-beam irradiation is applied to introduce cross-linking between polymer molecules since cross-linking and degradation processes are simultaneously occurring in amorphous regions of polymers as an effect of electron irradiation. Therefore, electron-beam irradiation cross-linking can lead to the formation of a three-dimensional network, consequently improving the mechanical properties of the polymer materials, besides improving other properties [6-7].

The purpose of this study was to evaluate the effects of electron-beam irradiation on thermo-mechanical properties of PBT/Clay nanocomposite.

2. MATERIAL AND METHODS

2.1. Material

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 bentonite chocolate clay (Pegmatech Especialidades Tecnologicas Ltda.) as a powder with toluene swelling of 8 mL/g.

2.1.1 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 as a nanoclay.

2.1.2 Nanocomposites 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 wound up manually. Finally, the PBT/Clay nanocomposite (70:30 wt %) was pelletized by a pelletizer, fed into injection molding machine and specimens test samples were obtained.

2.2 Electron-beam Irradiation

Part of the materials obtained were irradiated with 70 kGy using a 1.5 MeV electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power), at room temperature, in air, dose rate 28.02 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters ‘‘CTA-FTR-125’’ from Fuji Photo Film Co. Ltd.

2.3 Characterization

2.3.1 Statistical analysis

The difference between the results for irradiated and non-irradiated samples were then statistically evaluated by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

2.3.2 Thermo-mechanical tests

Tensile tests (ASTM D 638) [8], flexural tests (ASTM D 790) [9] and heat distortion temperature (HDT) (ASTM D 648) [10] were performed in this work in order to evaluate the thermo-mechanical behavior of the materials studied.

2.3.3 MFI measurements

MFI measurements were determined with a Microtest extruder plastometer (ASTM 1238-04) in the conditions specified for PBT.

3. RESULTS AND DISCUSSION

3.1 Thermo-mechanical tests

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

Figure 1 shows the results of the tensile strength at break tests for both, PBT and PBT/Clay nanocomposite. As it can be observed there was a significant increase of ca. 60% in tensile strength at break of PBT due to clay addition alone ($p < 0.05$). On the other hand, the values for tensile strength at break for irradiated PBT and PBT/Clay samples decreased by 7 % and 4%, respectively, when compared with non-irradiated samples.

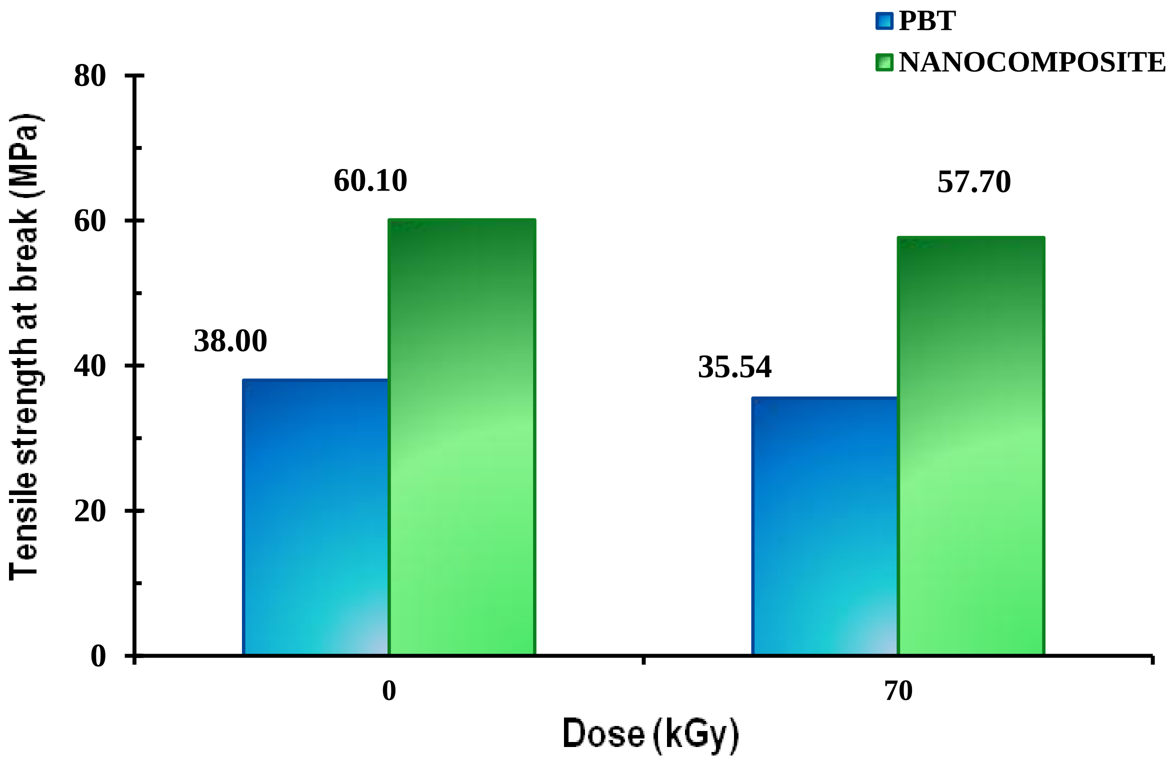

Figure 1. Tensile strength at break for PBT and PBT/Clay nanocomposite

The results of the elongation at break tests for both, PBT and PBT/Clay nanocomposite are given in Fig.2. As it can be observed, the elongation at break of PBT had a large reduction of about 87 % because of clay addition ($p < 0.05$). It can also be observed that the electron-beam radiation dose of 70 kGy caused a decrease in neat PBT elongation at break of around 30 %. No significant change in the elongation at break of irradiated PBT/Clay nanocomposite at the same radiation dose was observed when compared with non-irradiated samples.

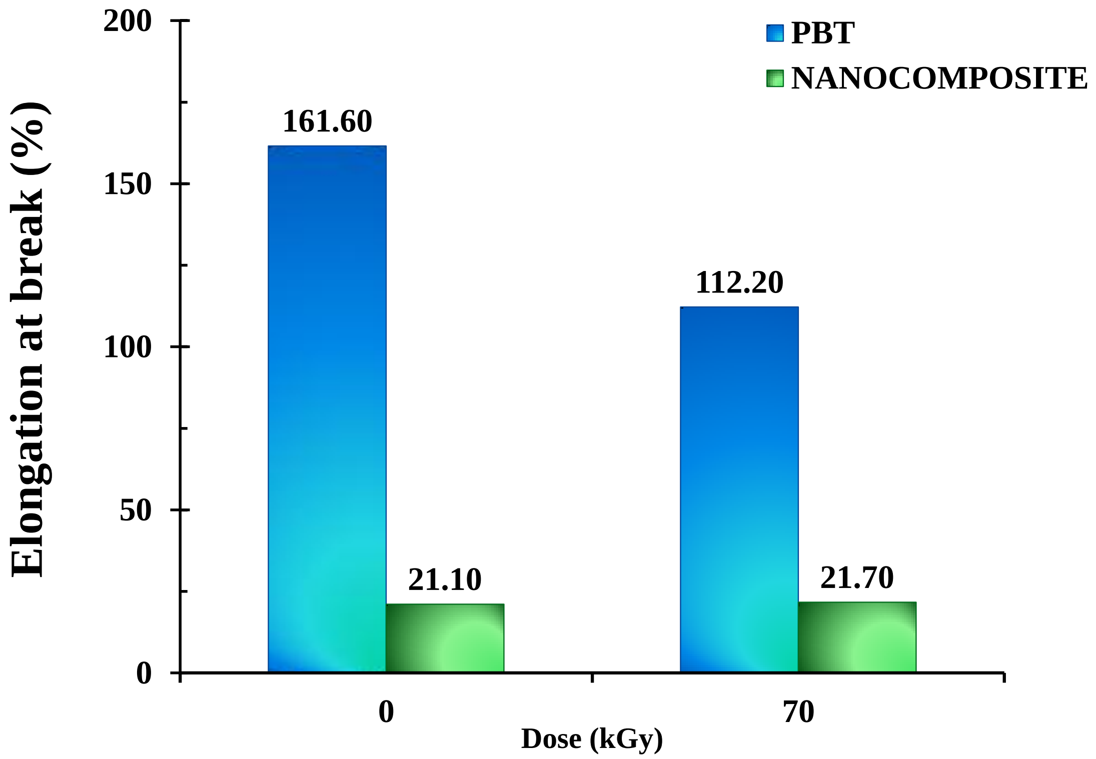

Figure 2. Elongation at break (%), for PBT and PBT/Clay nanocomposite

The flexural strength tests results for both, PBT and PBT/Clay nanocompostite are presented in fig. 3.

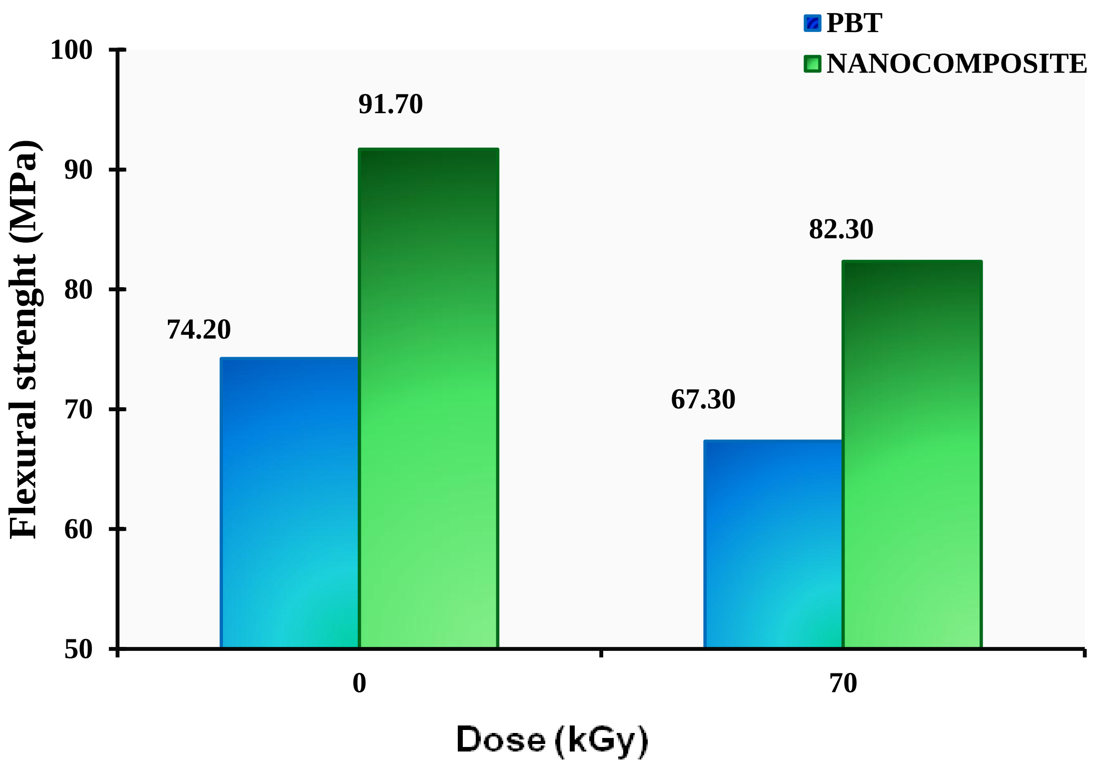

Figure 3. The flexural strength, for PBT and PBT/Clay nanocomposite

This figure shows that the flexural strength of PBT also presented a significant increase of around 25 % because of nanoclay addition alone. After electron-beam radiation dose of 70 kGy a significant reduction of around 10 % in this property can be observed for both, PBT and nanocomposite.

Figure 4 shows the results for flexural modulus tests. As it can be seen, there was a significant increase of ca. 15 % ($p < 0.05$) in flexural modulus of PBT due to the nanoclay incorporation alone. On the other hand, the values for flexural modulus for both, irradiated PBT and PBT/Clay nanocomposite, showed a slight decrease of around 3 %, and 4 %, respectively, when compared with non-irradiated samples.

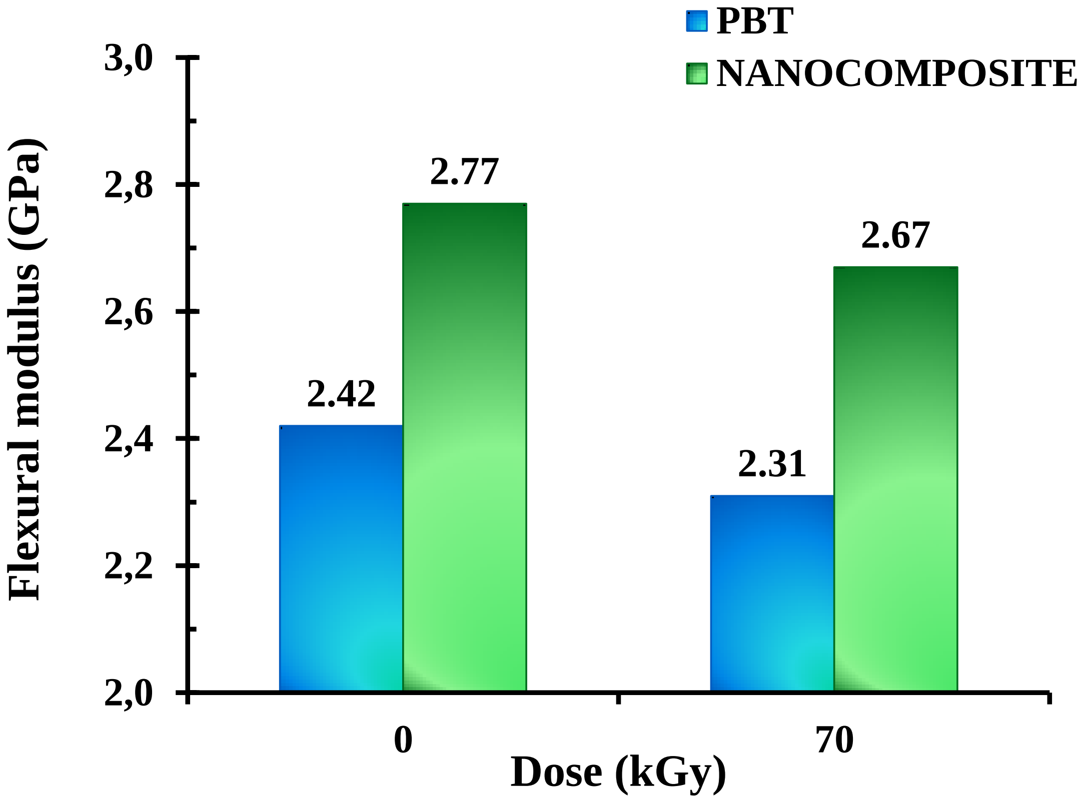

Figure 4. The flexural modulus, for PBT and PBT/Clay nanocomposite

In Fig. 5 Vicat testing results are presented, for both, PBT and PBT/Clay nanocomposite. This figure shows a slight tendency for an increase in Vicat softening temperature of PBT due to nanoclay incorporation and electron-beam irradiation treatment with 70 kGy.

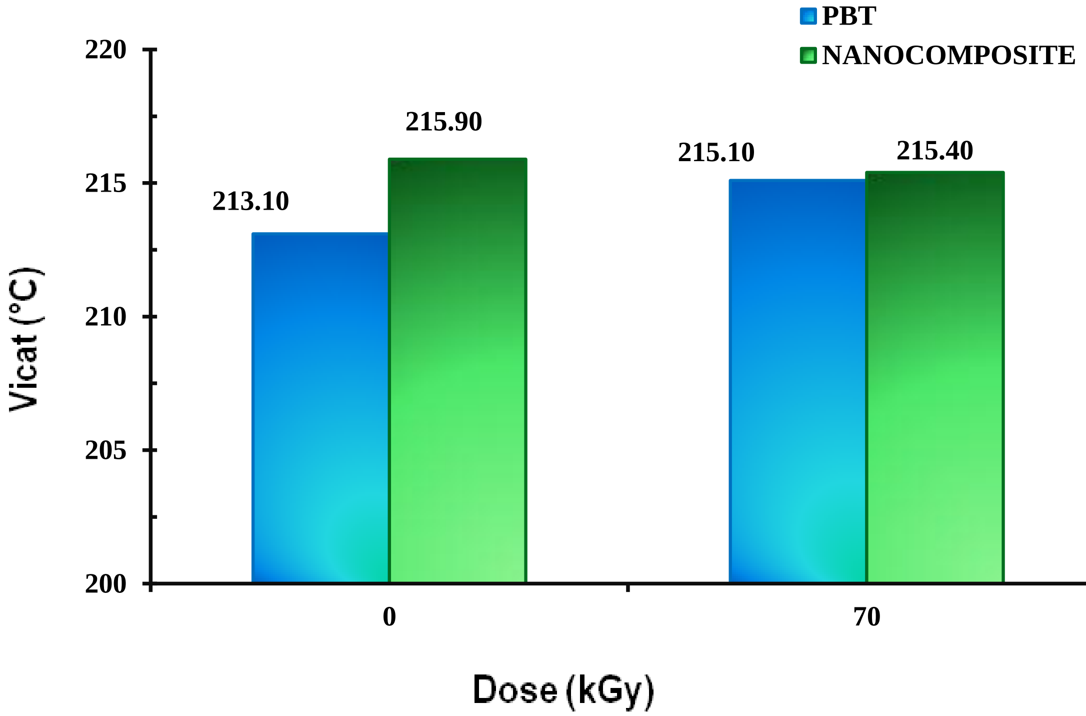

Figure 5. Vicat, for PBTand PBT/Clay nanocomposite

Figure 6 shows the Heat Distortion Temperature (HDT) for both, PBT and PBT/nanocomposite

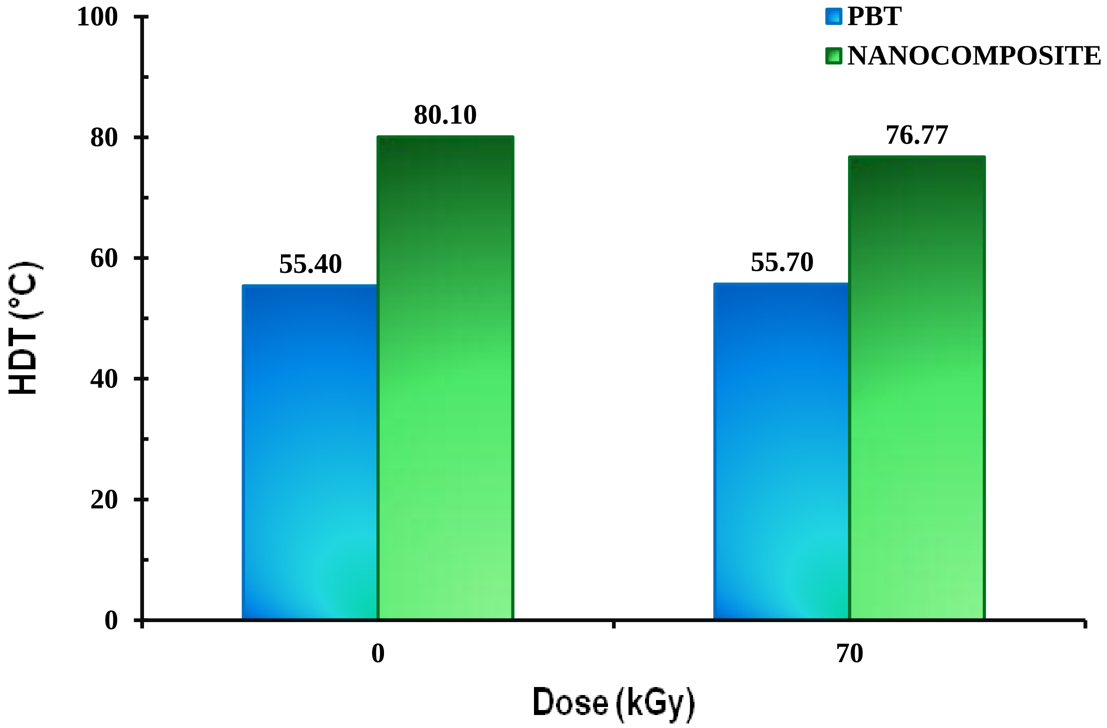

Figure 6. HDT, for PBT and PBT/Clay nanocomposite

Concerning HDT, the incorporation of nanoclay in PBT represented a gain of about 44 %. This figure also shows a small decrease for HDT of irradiated nanocomposite, while for irradiated PBT no significant change was observed.

The results for the MFI measurements of both, PBT and PBT/Clay nanocomposite are shown in the Fig. 7. It is important to highlight that there was a sharp increase of around 350 % as a result of the incorporation of nanoclay.
Considering that the melt flow index (MFI) is a measure of the plastic's ability to flow and it is inversely related to melt viscosity and to molecular weight of plastic, then the increase in MFI of nanocomposite in comparison with that of neat PBT may suggest that nanoclay addition led to the obtaining of a PBT/Clay nanocomposite with lower molecular weight and higher fluidity than PBT.

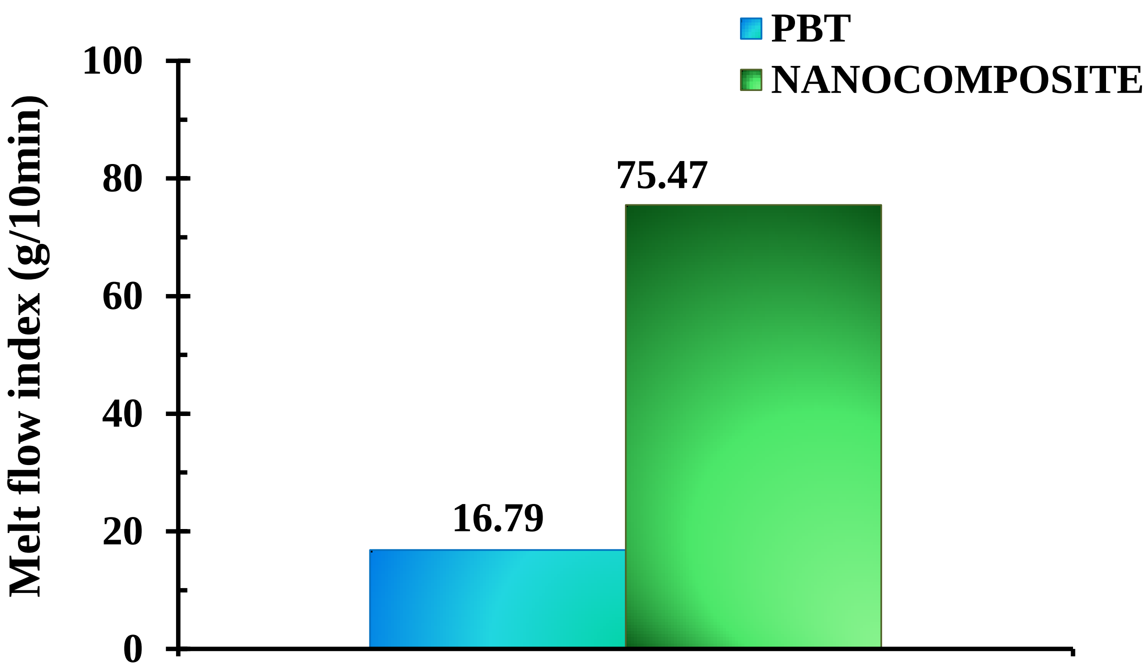

Figure 7. The MFI measurements of non-irradiated PBT and PBT/Clay nanocomposite

The superior thermo-mechanical properties of PBT/Clay nanocomposite observed in these results can be attributed to the degree of exfoliation and a good dispersion of clay layers in the PBT matrix, but further additional tests, such as XRD, TEM and SEM will be performed in order to confirm that. However, the reduction in these properties observed for both, PBT and nanocomposite, after electron-beam radiation treatment with 70 kGy suggest that radiation dose used did not make sufficient cross-linking among PBT chains.

4. CONCLUSION

The objective of the present study was to evaluate the contribution of the Brazilian smectitic clay (bentonite chocolate clay) and electron-beam irradiation in thermo-mechanical properties of PBT. The results showed that the incorporation of nanoclay represented a significant gain in tensile strength at break, flexural strength, flexural modules and heat distortion temperature (HDT) and a sharp increase in Melt Flow Index of the neat PBT. The electron-beam irradiation at radiation dose 70 kGy of PBT and PBT/Clay nanocomposite brings a small decrease in their properties. The superior thermo-mechanical properties of PBT/Clay nanocomposite observed in these study can be attributed to the degree of exfoliation and a good dispersion of clay layers in the PBT matrix.

ACKNOWLEDGMENTS

The authors wish to thank A. Schulman Brazil for providing the support for this work.

REFERENCES

1. M. Motomatsu, T. Takahashi, H.-Y. Nie, W. H. Mizutani and H. Tokumoto, Microstructure study of acrylic polymer silica nanocomposite surface by scanning force microscopy, Polymer, 38, 177-182, (1997).
2. J. Wen, J. E. Mark, Precipitation of silica-titania mixed-oxide fillers into poly(dimethylsiloxane) networks, Rubber Chem. & Tech., 67, 806-819 (1994).
3. Z. Pu, J. E. Mark, J. M. Jethmalani, W. T. Ford, Mechanical properties of a poly(methyl acrylate) nanocomposite containing regularly-arranged silica particles, Polymer Bulletin, **37**, 545-551 (1996).
4. K. Varlot, E. Reynaud, G. Vigier, J. Varlet, *Mechanical properties of clay-reinforced polyamide*, J Polym Sci Part B: Polym Phys, 40, 272-283 (2002).
5. "Wikipedia" http://en.wikipedia.org/wiki/Polybutylene_terephthalate
6. R. Buchalla, C. Schuttler, K.W. Bogl, *Effect of ionizing radiation on plastic food packaging materials: a review*, Part 1. Chemical and physical changes, J. Food Prot. v. 56, p. 991–997 (1993).
7. M. Bengtsson, K. Oksman, N. M. Stark, Profile *Extrusion and Mechanical Properties of Crosslinked Wood-Thermoplastic Composites*. Polymer Composites, 184-194 (2006).
8. American Society for Testing and Materials – ASTM, D 638 – 01, Standard Test Method for Tensile Properties of Plastics (2001).
9. American Society for Testing and Materials – ASTM, D 790 – 00, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials (2000).
10. American Society for Testing and Materials –ASTM D 648 – 07, Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position (2007)