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Irradiation of Pseudoboehmite-Polypropilene Nanocomposites

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Abstract. Polymeric nanocomposites are hybrid materials, where inorganic nanoscale dimensions substances are dispersed in a polymeric matrix. The fillers have a high surface area, promoting better dispersion in the polymeric matrix and therefore an improvement in physical properties of the composite depending on the homogeneity of the material. The preparation of nanocomposites polymer matrix allows in many cases to find a relationship between low cost due to the use of a lower amount of charge, and a high level of performance. In the present work, nanocomposites of polypropylene with different concentrations of pseudoboehmite obtained by a sol-gel process, and treated with octadecylamine were prepared. After preparation, the samples were irradiated with a 0, 50, 100, 200 e 300kGy radiation dose in an electron accelerator. The pseudoboehmite nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, differential thermal analysis and thermogravimetric analysis. The nanocomposites were characterized by thermal and mechanical tests. The addition of pseudoboehmite promoted a reduction of the melting flow during the production of the composites evidencing the interaction of pseudoboehmite with the polymeric matrix. Because the polypropylene is a semicrystalline polymer, when exposed to the irradiation process, their morphology was modified due to scission mechanisms of the polymer chains.

Introduction

Polyolefins are thermoplastics with a low cost and a huge range of properties and applications. However, these polymers exhibit properties much lower than engineering thermoplastics, with restrictions in their applications that require higher quality artifacts. In view of this, the addition of fillers is an alternative to overcome these limitations [1,2], since all the hybrid organic-inorganic composites generally exhibit mechanical properties superior to those of their pure components [3].

With the development of synthesis techniques and the possibility of characterization of materials at the atomic scale, it has become possible to incorporate nanoparticles in polymers with high surface area and that can significantly improve the properties of polymeric resin making it a material with higher mechanical strength, better thermal properties or superior chemical, electrical, optical or magnetic properties while improving the properties of flame resistance, and barrier properties. Furthermore, nanometric particles encourages greater interaction with the polymer matrix allowing, in many cases, the use of a smaller amount of filler to a high level of performance because of the synergy between the components of the resulting nanocomposite [4].

One successful process to achieving nanoparticles is the sol-gel process [5,6].

In this work a nanocomposite was prepared of polypropylene and a fine ceramic material, namely pseudoboehmite modified with octadecylamine. Pseudoboehmite is based on a monohydroxide aluminum oxide produced from the sol-gel synthetic route using ammonium hydroxide and aluminum nitrate as precursors. The octadecylamine is used like an organomodifier agent in organopseudoboehmite production.

These composites were characterized by the following techniques according to ASTM Standards: melt index, tensile strength, Izod impact, Vicat softening point, Deflection Temperature (HDT) and Shore D Hardness.

Experimental

The pseudoboehmite was produced by a sol-gel process according to that described in a previous paper [7, 8], with (Al(NO3)3.9H2O) (980g aluminum nitrate/1 L water), NH_4OH water solution (28wt%) and polyvinyl alcohol ([C2H4O]n; PVAl) solution (8 wt% in water) to increase the viscosity.

Posteriorly, the pseudoboehmite was impregnated with 0.8wt% of octadecylamine according to the procedure of reference 9.

The composites samples were obtained with polypropylene homopolymer supplied by Basell Poliolefina Ltda, contend different concentrations of 0, 1.0 and 3.0 wt.% of the pseudoboehmite treated with octadecylamine.

After preparation, the samples were irradiated at room temperature with an electron beam, using a Dynamitron electron accelerator with energy of about 1.5MeV, with doses of 0, 50, 100, 200 e 300kGy, and dose rate of 11.3 kGy/s.

Characterization methods for the pseudoboehmite

X-rays powder diffraction: for the samples dried at 70°C/24 hour's diffraction data were recorded with a Rigaku MultiFlex diffractometer with a fixed monochromator. The experimental conditions were: 40kV, 20mA, $20° < 2\theta < 100°$, $\Delta 2\theta = 0.02°$, λCuKα at room temperature. The collected data were compared with the ICDD data.

Scanning electron microscopy: scanning electron microscopy (SEM) images were taken with Phillips XL30 equipment using a secondary electron detector. The powder was placed upon SEM stubs covered with double-face tape and with gold in an Edwards Sputter Coater model S150B. The images were registered under magnifications of 200X and 6000X.

Thermal analyses: the thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed in a Netzsch-STA409C equipment; heating from room temperature to 1300°C, with 10°C min^{-1} heating rate, 50cm^3/min nitrogen.

Characterization methods for the polypropylene/pseudoboehmite composites

The mechanical measurements were performed in the samples at room temperature. The notched Izod Impact strength, tensile strength and Shore D Hardness were determined according to ASTM D256, D638 and D-2240, respectively. The Shore D Hardness was obtained using Mitutoyo Hardmatic equipment. The Vicat softening point (ASTM D1525) and Deflection Temperature data (HDT) were obtained according to ASTM D648 and was determined using Tinius Olsen HD94/398 equipment. The melt index was obtained according to ASTM D1238.

Results and discussions

Pseudoboehmite: Fig. 1 and Fig 2 show the data obtained in the X-ray diffraction and DSC tests. The X-ray diffraction data, in Fig. 1, shows the typical pseudoboehmite diffraction pattern with low intensity peaks observed, for example, at 2θ =13Åã (020) and 28Åã (021).

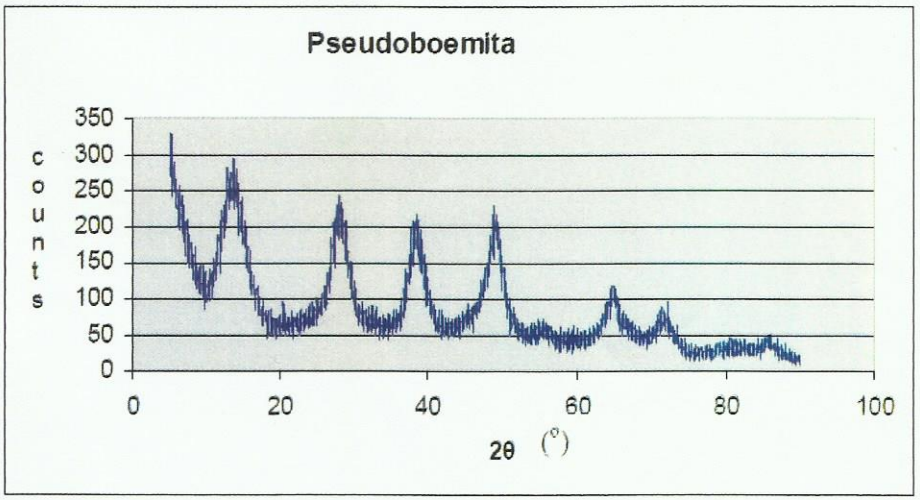

Figure 1. X-ray diffraction pattern of the pseudoboehmite

A typical curve of the DSC for pseudoboehmite (Fig.2) shows an endothermic peak near the temperature of 100°C, due to water vaporization. The transformation of pseudoboehmite to γ-alumina and the decomposition of PVAl in the same range temperature of the DSC analysis show a complex peak in the range of 200-400°C. The TG analysis shows the loss of weight corresponding to these phenomena. In the DSC analysis at around 1200°C is observed a peak attributed to the transformation of the last meta-stable phase of alumina to α-alumina.

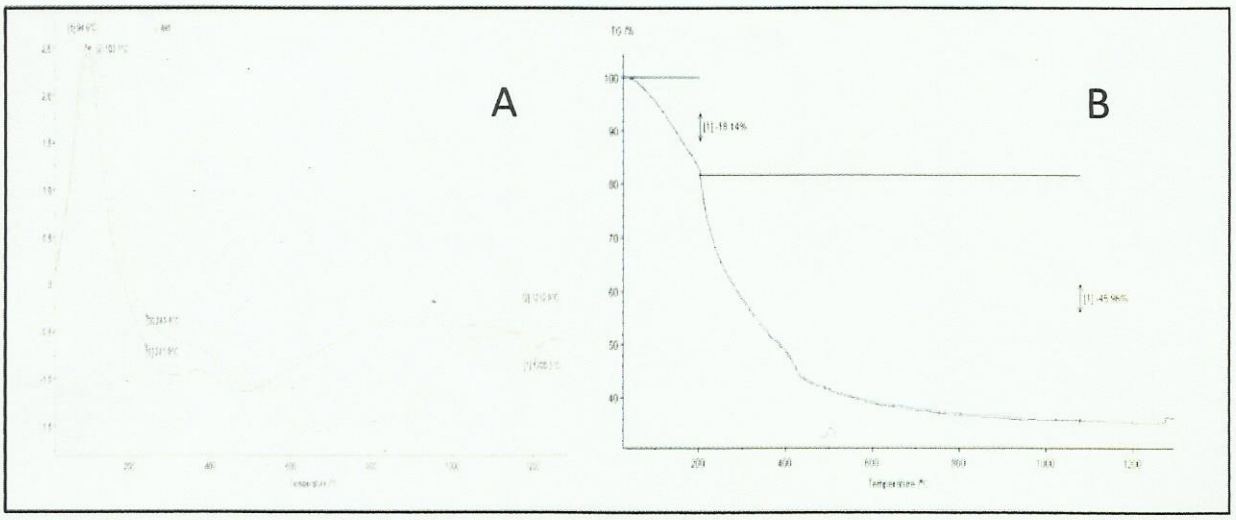

Figure 2. A) DSC for pseudoboehmite. B) TG analysis for pseudoboehmite.

Fig. 3 shows the scanning electron microscopy of pseudoboehmite obtained. The material surface has a high porosity level, as can be seen through the SEM analysis,

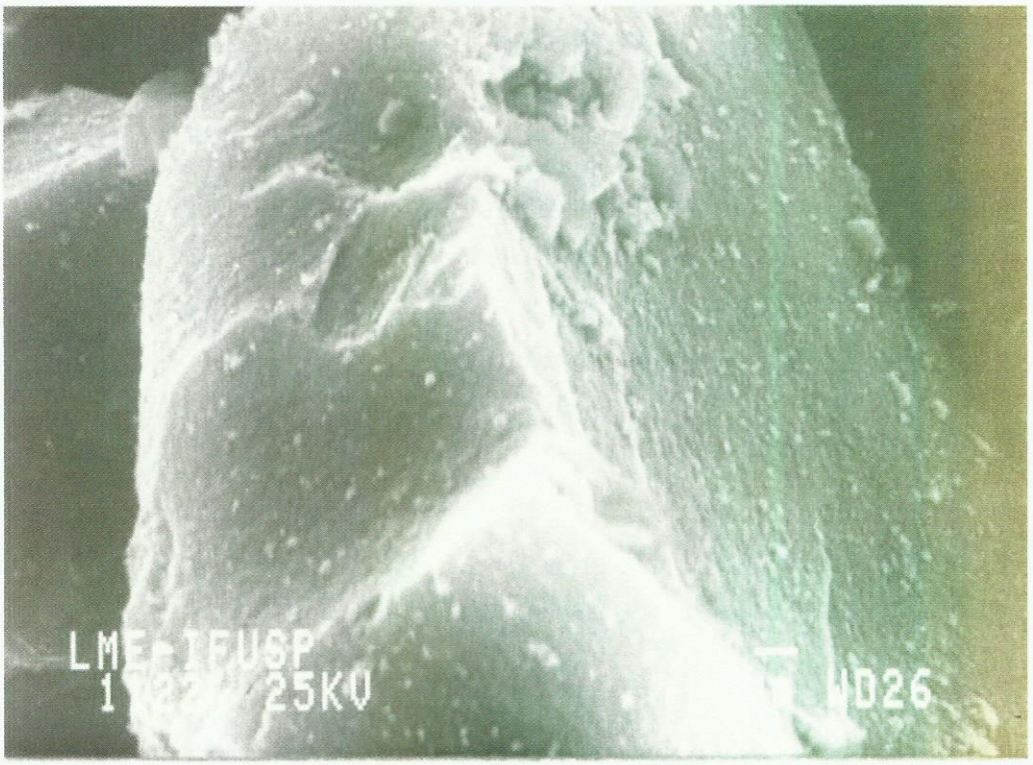

Figure 3. Scanning electron microscopy of the pseudoboehmite

Polypropylene/Pseudoboehmite Composites: The results of the melt index by the specimen show that the addition of pseudoboehmite increased the melt index results (Fig. 4).

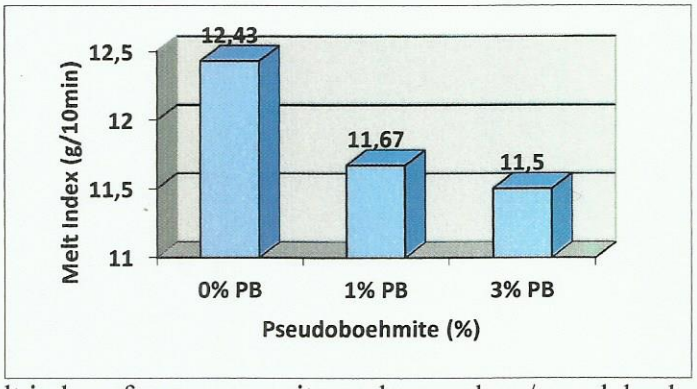

Figure 4. Melt index of nanocomposites polypropylene/pseudoboehmite samples.

The results of the impact energy absorbed by the specimens during failure show that the addition of pseudoboehmite decreased the Izod test results. The higher the dose of irradiation cause a decrease in impact strength of the composites, which can be explained by the scission of the chains of polypropylene process due to the radiation action (Figure 5).

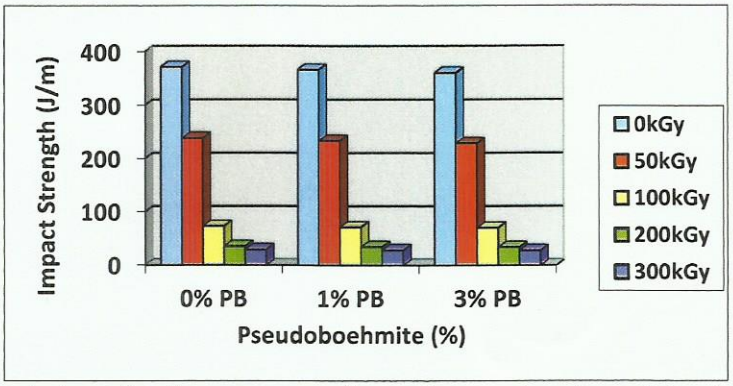

Figure 5. Impact strength of nanocomposites polypropylene/pseudoboehmite samples.

The pseusoboehmite presence in small amount (1.0 wt.%) causes a small increase in tensile strength, but this increase is not significant. For higher concentrations (3.0 wt.%) the presence of peseudoboehmite promotes a decrease in tensile strength. The tensile strength decreases with the action of ionizing radiation due to the breakup of polypropylene molecules (Fig. 6)

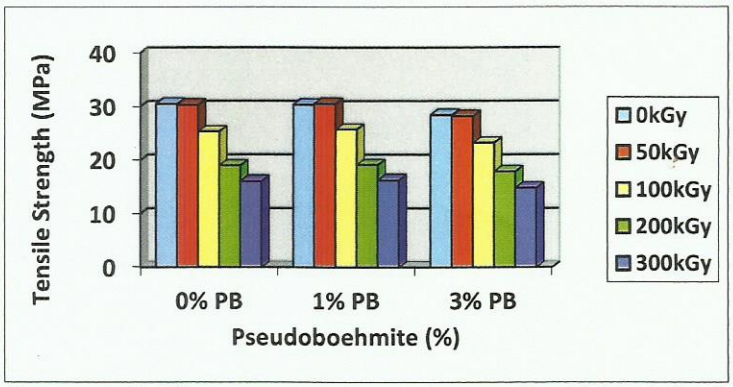

Figure 6. Tensile strength of nanocomposites polypropylene/pseudoboehmite samples.

The Shore D hardness data (Figure 7) shows that the samples containing the larger amount of pseudoboehmite (3%) show an increase in the Shore D hardness. The radiation cause an increase in Shore D hardness of the composites obtained until 100kGy, above this dose, the Shore D hardness results decrease.

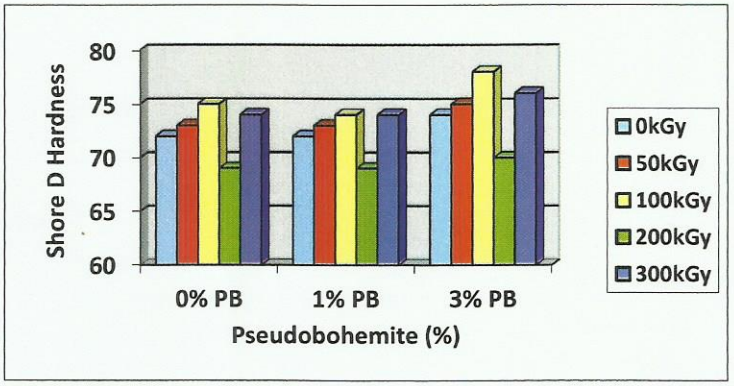

Figure 7. Shore D hardness of nanocomposites polypropylene/pseudoboehmite samples.

Examining the results for the thermal properties: HDT and Vicat softening temperature was observed that the pseusoboehmite presence makes little difference in these properties, with a small increase to the 1.0 wt.% pseusoboehmite concentration. At a concentration of 3.0 wt.%

pseudoboehmite the values are almost the same as the matrix without nanofiller addition. Radiation action causes a decrease in both the HDT as the Vicat softening temperature (Figures 8 and 9).

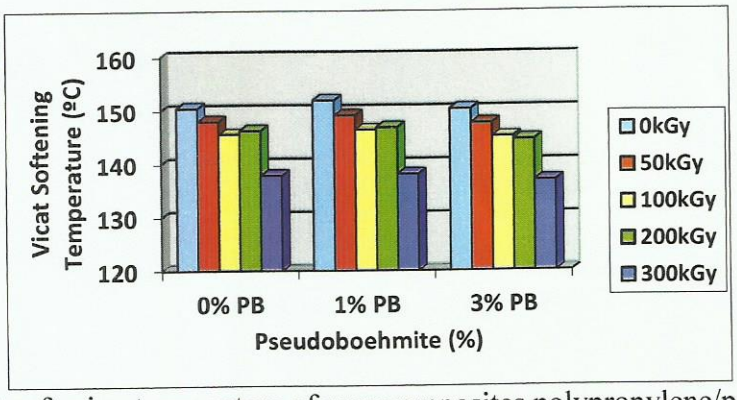

Figure 8. Vicat softening temperature of nanocomposites polypropylene/pseudoboehmite samples.

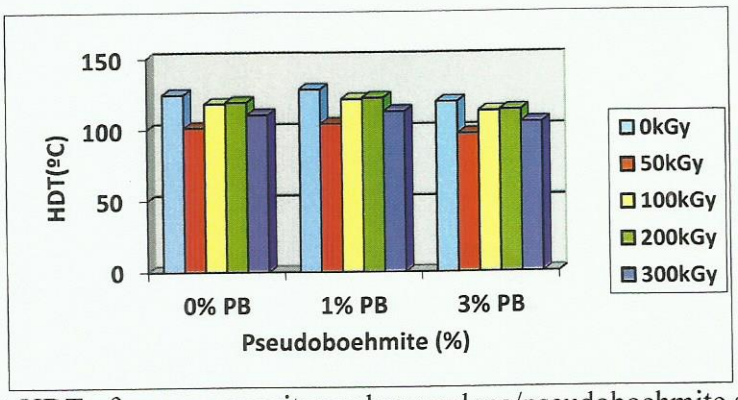

Figure 9. HDT of nanocomposites polypropylene/pseudoboehmite samples.

Conclusions

The X-ray diffraction data and DSC analysis show the typical results for pseudoboehmite, as related in the literature, and the scanning electron microscopy shows that the product of the sol-gel synthesis is a very porous material.

The addition of pseudoboehmite/octadecylamine at 1.0 wt% promoted a small increase in the thermal and mechanical properties, while the addition at 3.0 wt% promote a decrease.

The irradiation process promotes scission of the polypropylene chains causing a decrease in thermal and mechanical properties of the nanocomposites.

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