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Characterization of Polystyrene Nanocomposites Containing Nanoparticles of Pseudoboehmite Obtained by Sol-Gel Process

Leila Figueiredo de Miranda[1, a *], Leid Jeane Pastrolin Goulart[1,b], Leonardo G. de Andrade e Silva [2,c], Alexandre Crioruska Donadon [1,d], Fabio Yuji Yamasaki [1,e], Antônio Hortêncio Munhoz Júnior[1,f,*]

[1] Universidade Presbiteriana Mackenzie – U.P.MACKENZIE – Rua da Consolação, 930 – Cep 01302-907 - Consolação - São Paulo - SP – Brazil

[2] Instituto de Pesquisas Energéticas e Nucleares – IPEN – São Paulo - SP - Brazil

[a]leila.miranda@mackenzie.br; [b]engmateriais@mackenzie.br; [c]lgasilva@ipen.br; [d]engenharia@mackenzie.br; [e]acdonadon@mackenzista.br; [f]ahmunhoz@yahoo.com

* corresponding author

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Abstract. Polymeric nanocomposites are hybrid materials in which inorganic substances of nanometric dimensions are dispersed in a polymeric matrix. These inorganic substances have high surface area allowing a better interaction with the polymeric matrix and consequently promote changes in the physical properties of the final composite with small additions of the same. The preparation of nanocomposites with polymer matrix allows in many cases to find a relationship between a low cost due to the use of lower amount of charge, reaching high level of performance. In this work, it was obtained polystyrene nanocomposites with pseudoboehmite synthesized by the sol-gel process with different concentrations of pseudoboehmite using and not using octadecylamine as a coupling agent. The nanocomposites were prepared by the melt intercalation technique. The pseudoboehmite nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, differential thermal analysis and thermo gravimetric analysis. The nanocomposites were characterized by differential thermal analysis, thermogravimetric analysis, heat deflection temperature, Vicat softening point, mechanical and rheological tests. The results showed an increase in the thermal properties, hardness and tensile strength values and decrease in the melt index, impact resistance and tensile elongation, showing the interaction of the filler with the polymer matrix. Although in the samples with the presence of octadecylamine the data shows that the thermomechanical properties practically do not vary in relation with the samples without octadecylamine.

Introduction

The great interest in the development of research involving polymers aims to significantly increase product quality, and polymer nanocomposites have attracted great interest from both academia and industry because they have physicochemical properties different between the micro and macrocomposite [1].

When compared with pure polymers, polymer nanocomposites containing from 1 to 6% by weight of material having at least one three-dimensional nanoscale present a range of different properties such as barrier properties, increase modulus, tensile strength, flame retardancy, corrosion resistance, heat resistance, amongst other properties [2, 3].

Polystyrene is a thermoplastic polymer, amorphous, transparent, hard and easy processing. This material may be found in several ways, the most common is the atactic polystyrene also known as "General Purpose (GP)" or crystal polystyrene [4]. It presents as shiny, colorless and odorless, has good optical and electrical properties, good dimensional stability and low moisture absorption. The ease of production and processing, and its low cost are other advantages of this polymer. However,

it presents some limitations, such as limited resistance to radiation, low resistance to temperature. Moreover, despite its rigidity, it becomes brittle when subjected to long storage periods.

Pseudoboehmite obtained by the sol-gel process is a ceramic material with high specific surface area and manometric characteristics, which presents numerous applications, it may be added to other materials to improve their thermomechanical properties [5, 6, 7].

To obtain polymer nanocomposites containing ceramic nanoparticles with suitable properties is needed, in most cases, adding a coupling agent to compatibilize the organic and inorganic phases. Among these coupling agents that cause compatibility between the polymeric material and the ceramic material is octadecylamine (ODA) [8, 9, 10, 11].

In this work, the thermo-mechanical properties were studied of the PS nanocomposites obtained by melt, containing pseudoboehmite obtained by the sol-gel process using ODA as a coupling agent.

Experimental

Pseudobohemite Synthesis: The pseudoboehmite was produced by the sol-gel process according to the method described in a previous paper [12, 13]. The reagents used were: $Al(NO_3)_3.9H_2O$ (980g aluminum nitrate/1 L water), ammonium hydroxide (NH_4OH) 28wt% water solution and polyvinyl alcohol ($[C_2H_4O]n$) solution (12 wt% in water), which was used to increase the viscosity. The volume ratio of aluminum nitrate solution to polyvinyl alcohol solution was 2.5:1. The aluminum nitrate solution was mixed with the polyvinyl alcohol and the mixture was dropped into an ammonium hydroxide solution. After that, the product was aged at 130°C in an autoclave for 24 hours.

The product of the synthesis was filtered and washed with deionized water during filtration.

Thereafter the product of filtration was dried at 70°C for 24 hours in air.

All chemicals used in the experiments are of Analytical Reagent grade and were used directly without any further purification. All the solutions were prepared with deionized water.

Posteriorly, the obtained pseudoboehmite was impregnated with 0.8wt% of octadecylamine according to the procedure of Zapata et al. (2010) [14].

Nanocomposites: The samples were obtained with crystal polystyrene (POLYSTYROL 158K) supplied by UNIGEL, containing different concentrations of pseudoboehmite treated with octadecylamine (ODA): 0, 1.0 ; 3.0 and 5.0 wt.%.

Characterization methods for the pseudoboehmite

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

Thermal analysis (thermogravimetry): The thermogravimetry of pseudoboehmite was obtained in a Netzsch-JupiterSTA449F3 equipment with heating from room temperature to 1300°C at 20°C min^{-1} and 50cm^3/min N_2 flow.

Characterization methods for the polypropylene/pseudoboehmite nanocomposites: 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. Thermogravimetric analyzes were performed according to ASTM D3850.

Results and discussions

Pseudoboehmite: The X-ray diffraction data, in Fig. 1, shows the typical pseudoboehmite diffraction pattern with low intensity peaks observed, for example, at 2θ =13o (020) and 28o (021). The results were compared with the data obtained by Moroz et al. [15].

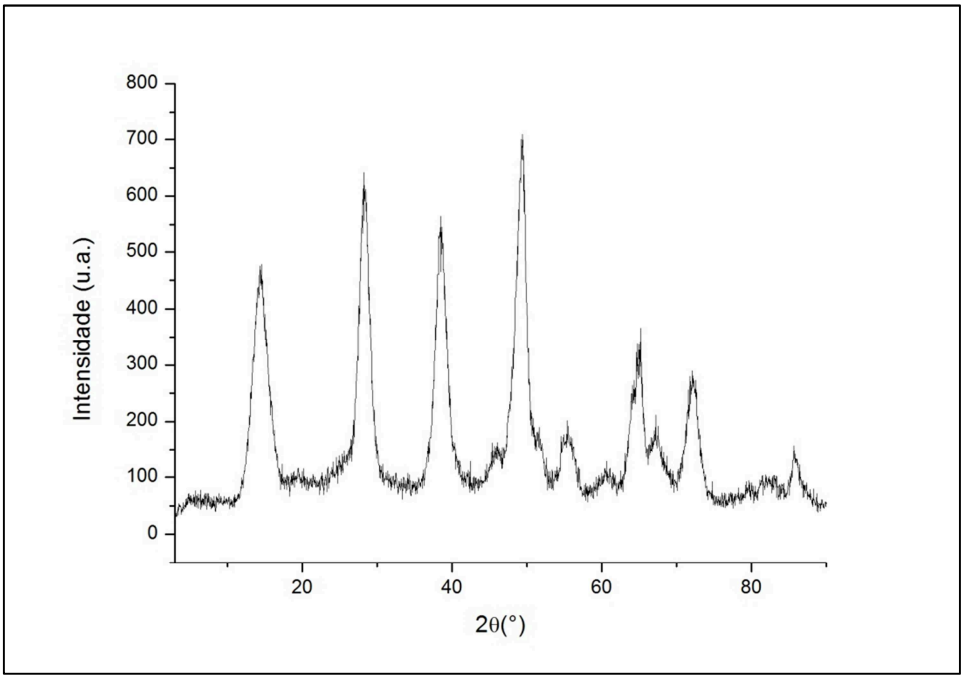

Fig. 1: X-ray diffraction data of synthesized pseudoboehmite.

By the pseudoboehmite thermal analysis (thermogravimetry) (Fig. 2 and Fig. 3) is observed that at around 100°C there is a mass loss that is associated with water. Around 200°C it is observed mass loss associated with decomposition and polyvinyl alcohol and, after that the pseudoboehmite transformation → γ- Al_20_3. It is also observed around 1200°C, the formation of the more stable phase of alumina, α-Al_2O_3. The sample thermal analysis is in agreement with literature data [16].

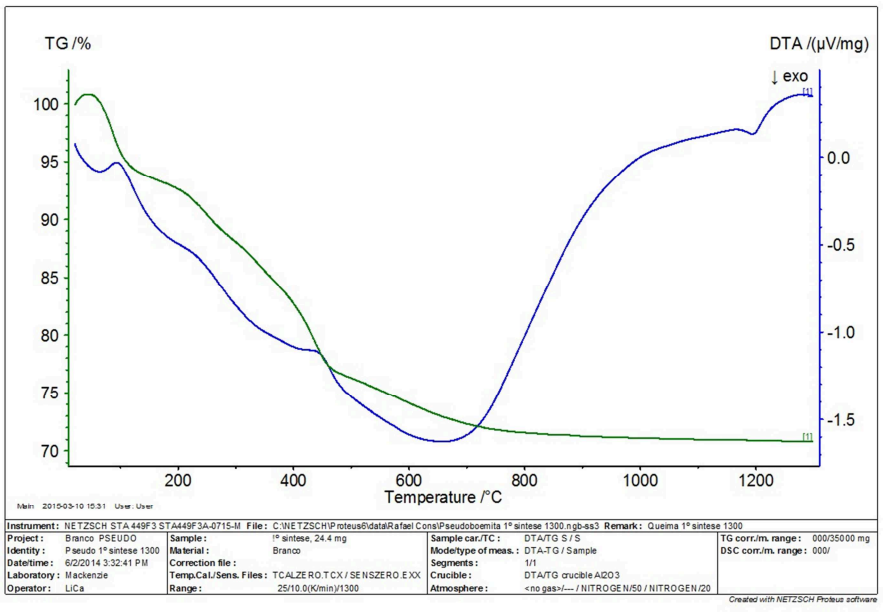

Fig. 2: DTA and TG obtained for the synthesized pseudoboehmite.

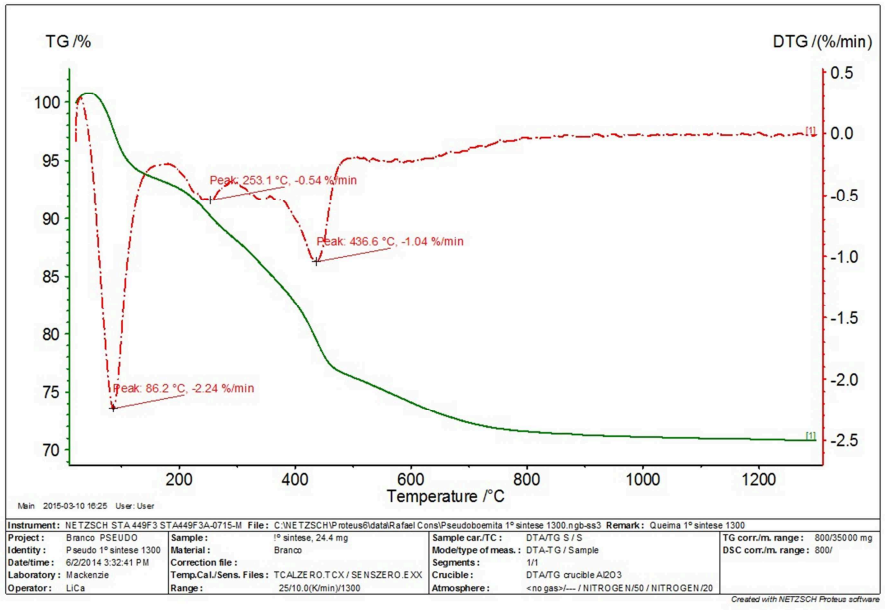

Fig. 3: TG and DTG obtained for the synthesized pseudoboehmite.

By the pseudoboehmite SEM (Fig. 4) shows that the product of the sol-gel synthesis is a very porous material.

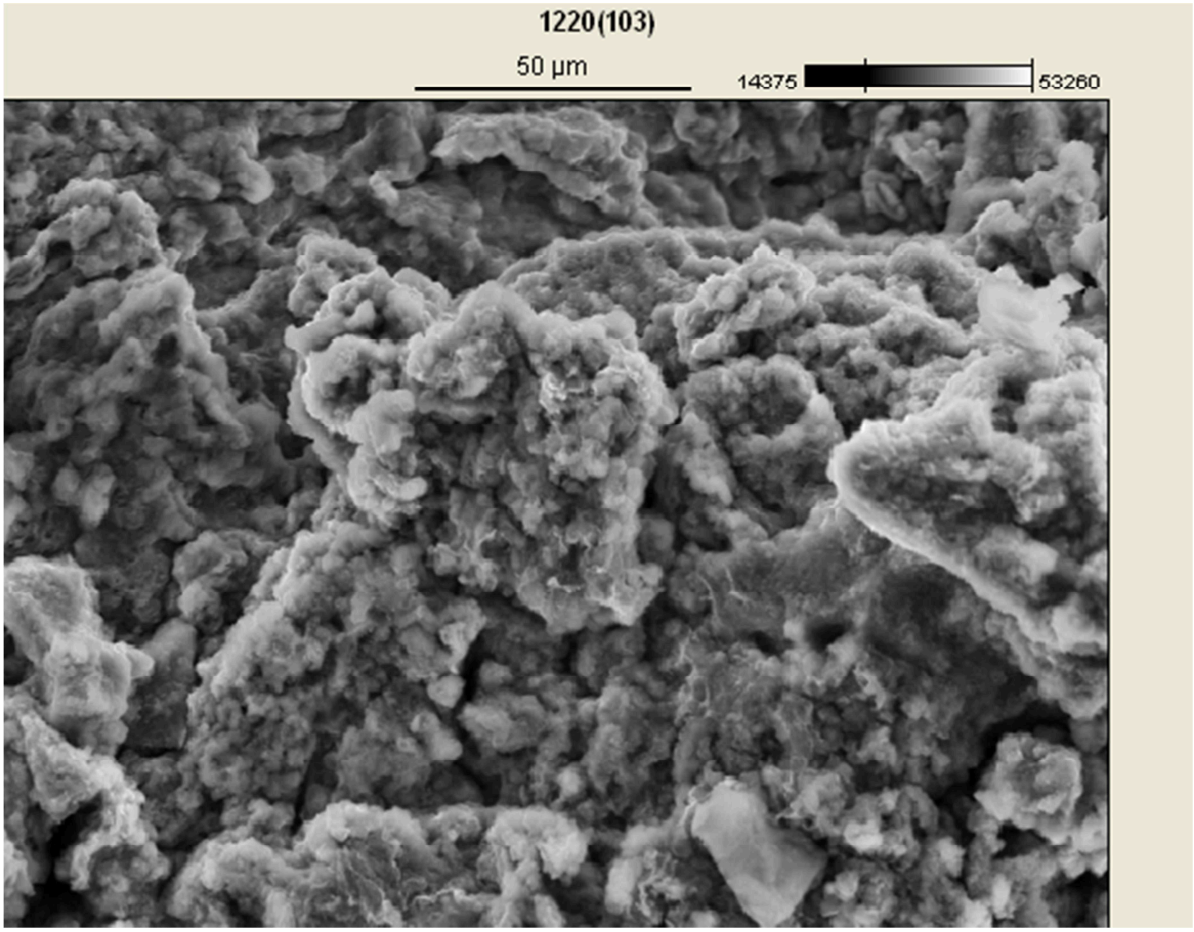

Fig. 4: SEM of pseudoboehmite obtained by sol-gel process.

Polystyrene/pseudoboehmite nanocomposites

Melt Flow index: The results to melt flow index tests are shown in the Fig. 5. It can be seen that the melt index decreases with the addition of pseudoboehmite. Probably occurs an interaction of pseudoboehmite with the polymeric matrix.

The results show that the melt index decreases slightly to the nanocomposites obtained with pseudoboehmite treated with ODA.

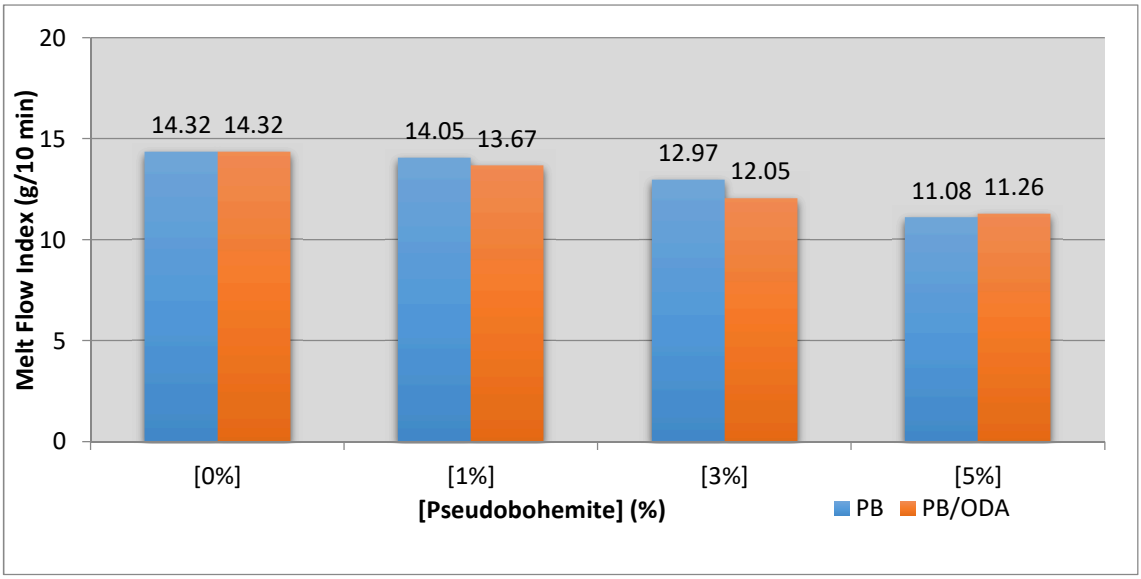

Fig. 5: Results to melt flow index tests.

Shore D Hardness: The results to hardness tests are shown in Fig. 6.

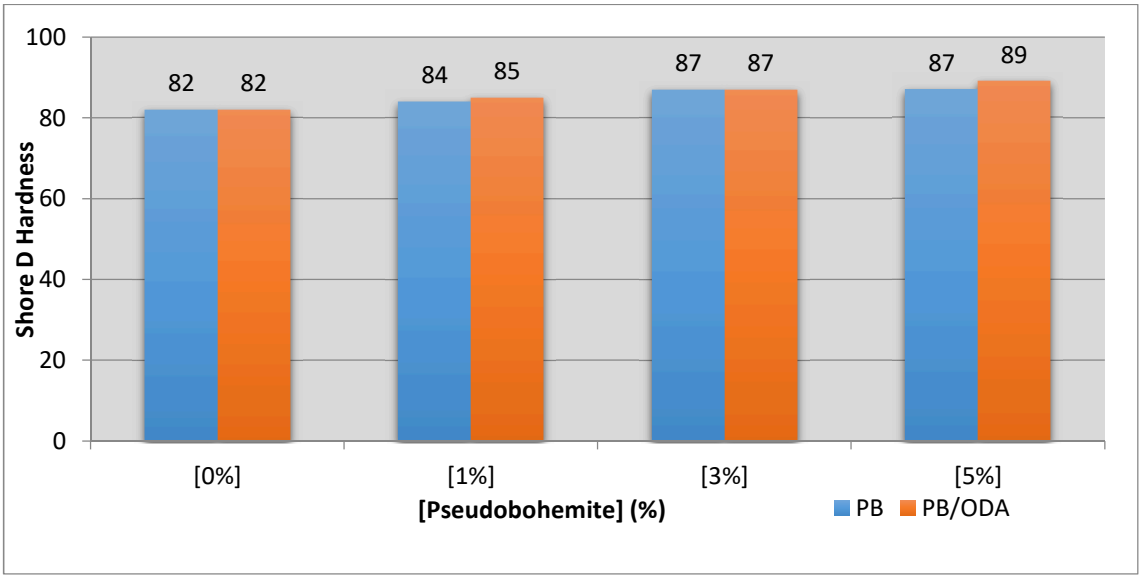

Fig. 6: Results of hardness tests.

By the obtained data, it was observed that:

- The addition of pseudoboehmite increases the hardness of the nanocomposites obtained. This increase is proportional to the concentration of pseudoboehmite in nanocomposite;
- The pseudoboehmite promotes closer ties between molecules, increasing the crystallinity of the material.
- The results show that the hardness does not change too much for nanocomposites obtained with pseudoboehmite treated and not treated with ODA.

Izod impact: Fig. 7 shows the results to Izod impact to samples obtained.

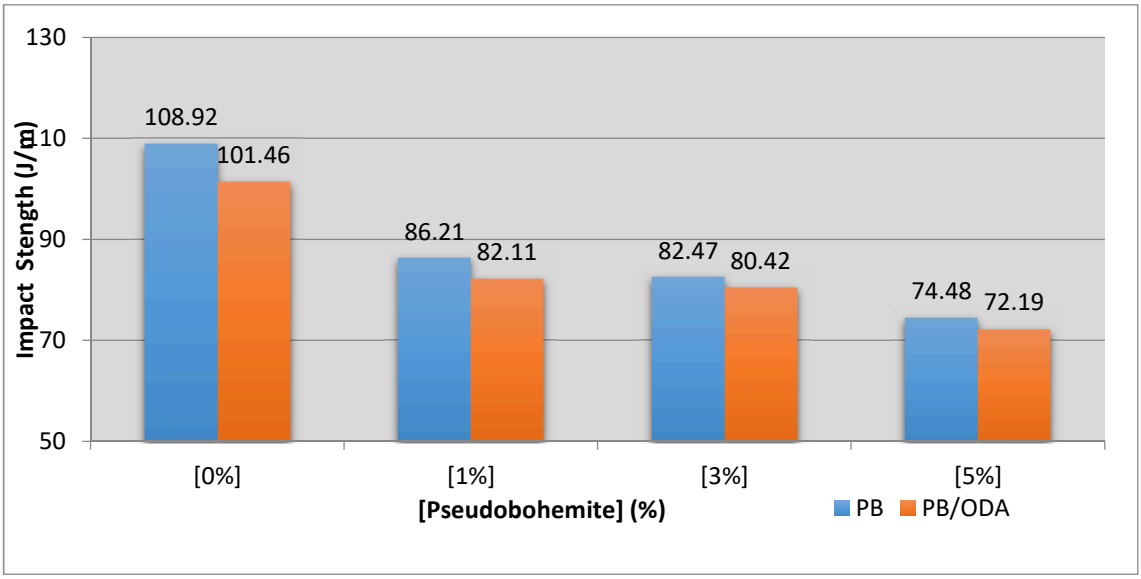

Fig. 7: Izod impact results.

By the results, it was observed that the addition of pseudoboehmite decreases the impact resistance. This decrease is proportional to the concentration of pseudoboehmite in the nanocomposites. The pseudoboehmite increases the stiffness of the material.

The presence of ODA causes a decrease in the impact Izod resistance, due to the increased interaction of pseudoboehmite and the polymeric matrix caused by the presence of coupling agent.

Tensile Strength: Figs. 8 and 9 shows the results to tensile tests to samples obtained. By the results obtained, it can be observed that the modulus of elasticity hardly changed, and no significant changes to the breaking strain. The presence of the coupling agent does not cause significant changes in the tensile properties.

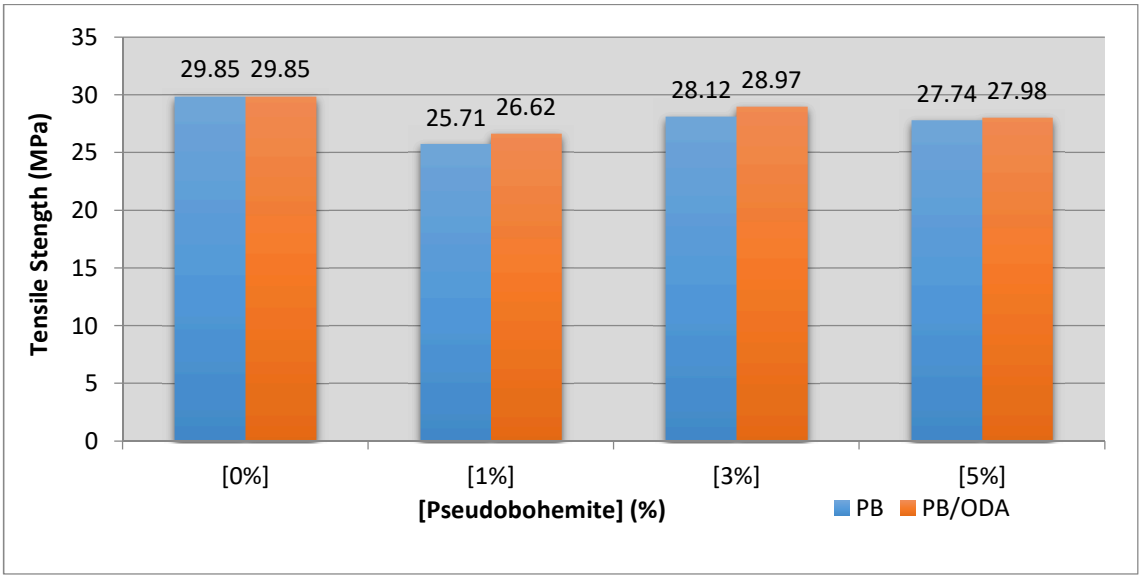

Fig. 8: Results to tensile strength in rupture.

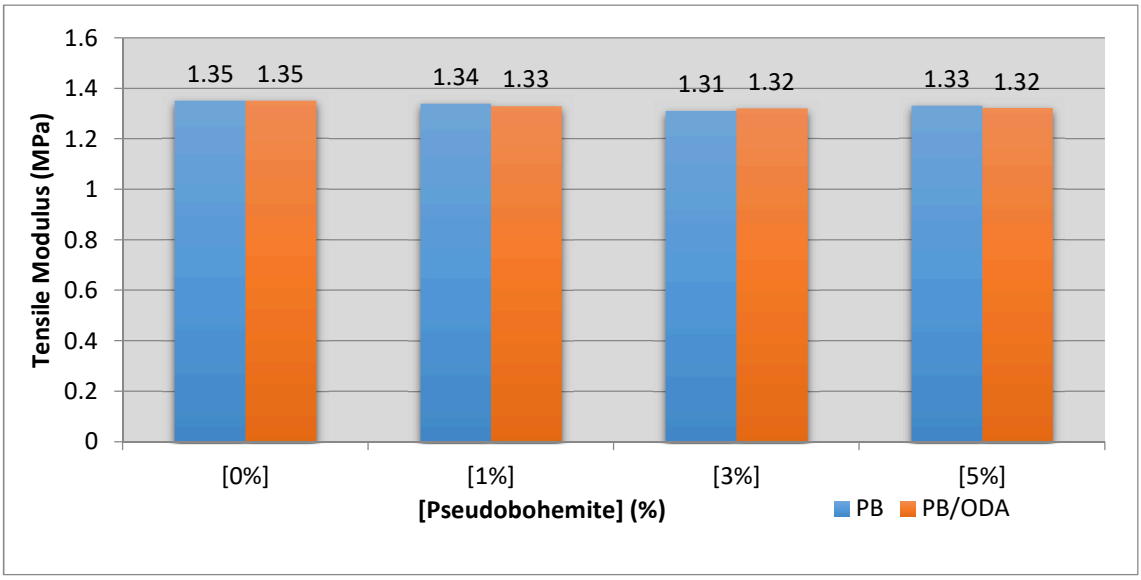

Fig. 9: Results to tensile modulus.

HDT and Vicat softening point: The Table 1 presents the results to HDT and Vicat softening point tests.

Table 1: Results to HDT and Vicat softening point tests.

	Wt% pseudoboehmite(PB)	HDT (°C)	Vicat softening point (°C)
PURE PS	0	83.76±0.28	90.84±0.10
PS+[PB] (%)	1	87.98±0.14	99.84±0.10
	3	89.75±0.19	99.75±0.27
	5	91.92±0.21	100,86±0,13
PS+[PB/ODA] (%)	1	88.22±0.14	102.94±0,12
	3	89.70±0.19	100.14±0.18
	5	91.80±0.21	101,85±0,20

By the results, it can be observed a slight increase in heat deflection temperature and Vicat softening point with the increase of pseudoboehmite in the nanocomposite. These results indicate an improvement in the thermal properties of the material produced due to the addition of pseudoboehmite. The presence of the coupling agent does not cause significant changes in the thermal proprieties.

DTA and Thermogravimetry: The DTA and thermogravimetry analysis (thermogravimetry) were done to pure PS and the nanocomposite containing 3.0wt% of pseudoboehmite not treated with ODA. By the nanocomposites thermal analysis (Figs. 10 and 11) it is observed that the nanocomposite thermal decomposition occurred at a higher temperature than the pure PS.

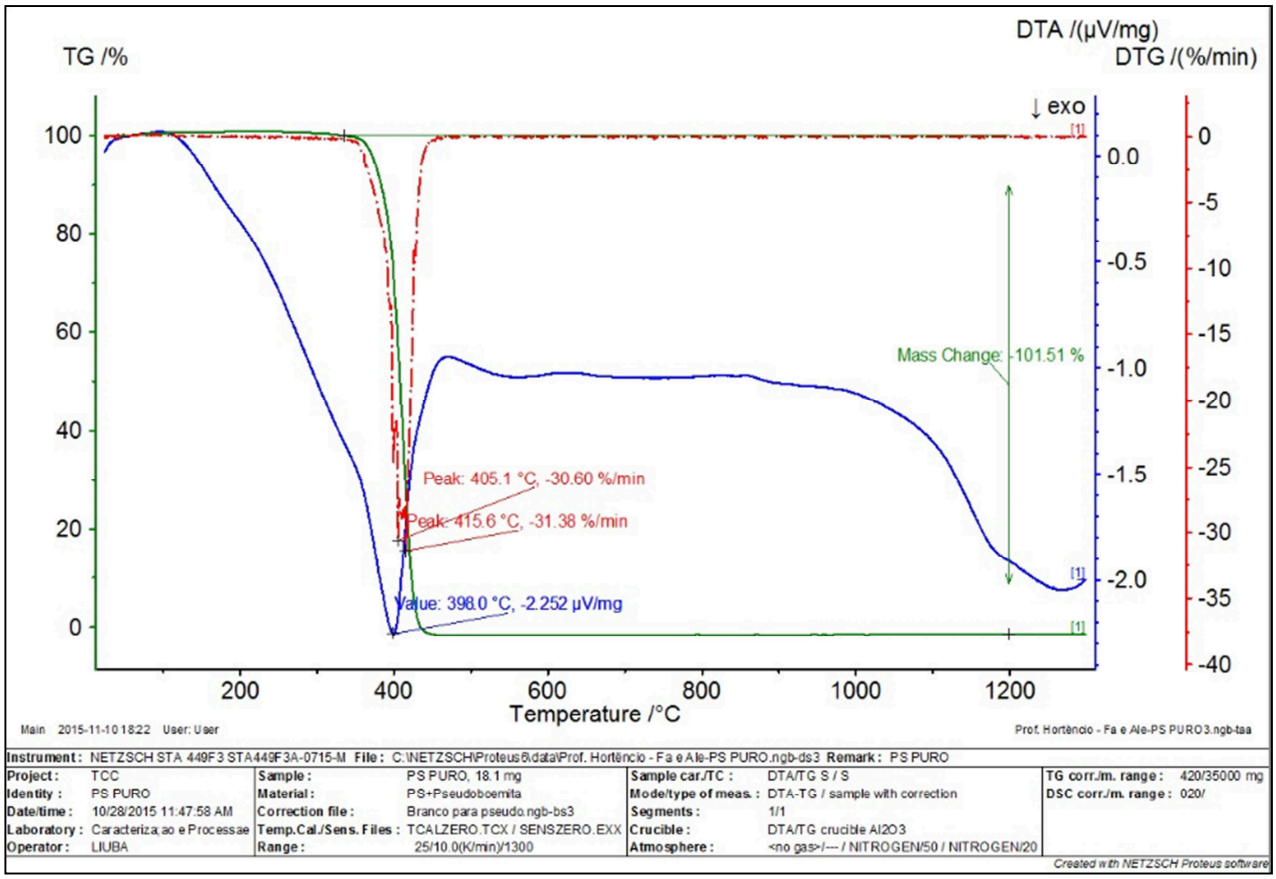

Fig. 10: Thermogravimetry analysis to pure PS.

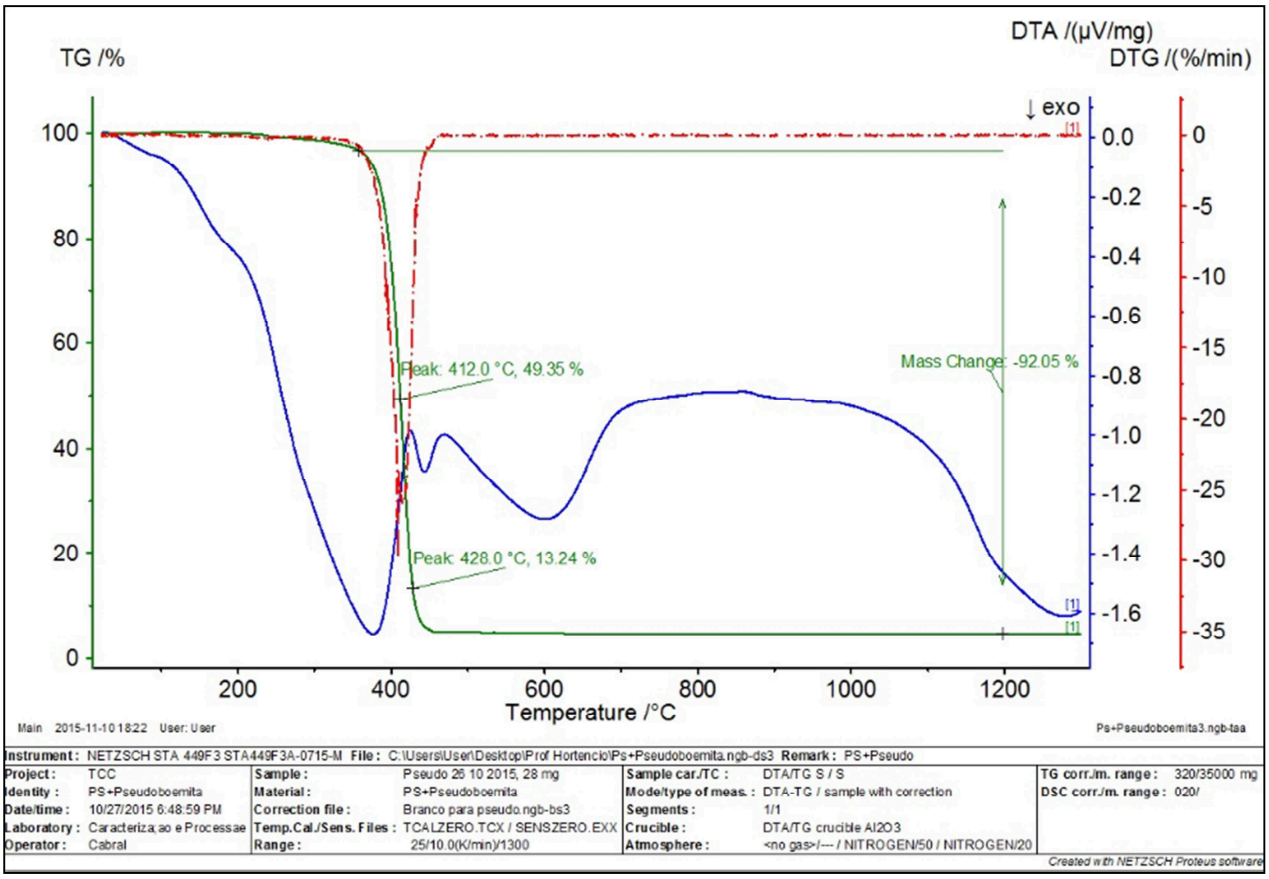

Fig. 11: Thermogravimetry analysis to nanocomposite containing 3.0wt% of pseudoboehmite.

Conclusions

In this work, we synthesized nanocomposite PS/pseudobohemite, treated and not treated with ODA.

In these conditions the addition of pseudoboehmite in the polystyrene incurs increases in the melt flow index and in the hardness of the nanocomposites obtained. Practically does not affect the tensile strength and modulus and the impact Izod strength decreases.

By the results, it can be observed that the presence of pseudoboehmite causes a slight increase in heat deflection temperature and Vicat softening point and the thermal decomposition occurred at a higher temperature than the pure PS. These results indicate an improvement in the thermal properties of the produced material.

Although the presence of octadecylamine causes greater interaction between the pseudoboehmite and polystyrene matrix, the thermomechanical properties practically do not vary with and without ocatadecylamine addition.

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