Characterization of a Composite of High-Impact Polystyrene, Pseudoboehmite and Graphene Oxide

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Abstract The application of a composite material of pseudoboehmite, polystyrene and graphene oxide was studied. The present work is the synthesis and characterization of high-impact polystyrene (HIPS) nanocomposite, with pseudoboehmite (PSB) and graphene oxide. Pseudoboehmite particles with nanometric dimensions were obtained by sol-gel process. The composites were characterized by mechanical tests (tensile strength, flexural strength, Izod Impact, Shore D Hardness), thermal (Flow index, temperature of thermal deflection under load-HDT, Vicat softening temperature, differential tests thermal analyses and thermogravimetric analysis) and morphologically by Scanning Electron Microscopy (SEM). The results obtained were compared with HIPS matrix properties, without PSB and graphene oxide addition. From the thermal analyzes, composite samples showed higher decomposition temperatures compared to pure high-impact polystyrene especially in the thermogravimetric analysis results, showing a considerable increase in the temperature at which material decomposition begins (322 °C for pure high-impact polystyrene and 380 °C for the composite).

Keywords High-impact polystyrene · Pseudoboehmite · Graphene oxide Nanocomposite

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Introduction

The performance of a composite material system is critically controlled by the interfacial characteristics of the reinforcement and the matrix material. The dispersion of nanoparticles in a matrix is also a very difficult task to ensure the uniform distribution of the nanoparticles in the final products. The production of polystyrene nanocomposites is actually studied. MgO-filled nanocomposites with enhanced high voltage resistance were developed on the basis of microwave transparent crosslinked polystyrene (CPS). The SEM images show that the distribution of MgO in the products was uniform, whereat the excellent mechanical properties of CPS were well maintained [1]. In other research, with the purpose to improve the flame resistance of polystyrene, three kinds of organophilic heterionic montmorillonites (Na-montmorillonite, Ca-montmorillonite, and Fe-montmorillonite) reinforced polystyrene nanocomposites were prepared by the melt dispersion method. The flame resistance of polystyrene/Na-montmorillonite nanocomposite was the best. The polystyrene/Camontmorillonite was the second in flame resistance, which is slightly better than that of polystyrene/Fe-montmorillonite [2].

Graphite oxides (GOs) with different oxidation degrees and graphene nanosheets (GN) were prepared by a modified Hummers method and thermal exfoliation of the prepared GO, respectively. Polystyrene (PS)/GO and PS/GN were prepared via melt blending. Cone calorimetry is one of the most effective bench-scale methods for studying the flammability properties of materials. The peak heat release rate (PHRR) value proves to be the most important parameter to evaluate fire safety. The nanocomposites (PS)/GO and PS/GN had a much lower PHRR than that of the virgin polymer.

The optimal flammability was obtained with the graphene (5 wt%), in which case, the reduction in the peak heat release rate is almost 50% as compared to PS [3].

Pseudoboehmite ($AlOOH \cdot xH_2O$), an oxyhydroxide compound, is an important crystalline phase in nature and industry [4, 5]. It is used as an alumina precursor in the production of nanocomposites and recently is also used with biopolymers [6, 7].

Graphene oxide (GO) is a giant model compound of polycyclic aromatic hydrocarbon oxides [8]. Recently, it was reported that graphite oxide can undergo complete exfoliation in water, yielding colloidal suspensions of almost entirely individual graphene oxide sheets [9].

High-Impact Polystyrene (HIPS) is a thermoplastic, produced by the addition of the styrene monomer. It is an easy-to-process and extremely versatile polymer widely used in the packaging industry. In this paper, a High-Impact Polystyrene nanocomposite with pseudoboehmite and graphene oxide was studied. The pseudoboehmite was used to disperse the graphene oxide in the polymer matrix.

Materials and Methods

Materials and Characterization of Pseudoboehmite

The pseudoboehmite gels were synthetized by sol-gel process using as precursors aqueous aluminum nitrate nine-hydrated ($Al(NO_3)_3 \cdot 9H_2O$) solution (950 g L^{-1}) and aqueous ammonium hydroxide solution (NH_4OH) (28 wt%). The graphene oxide was dissolved in the aluminum nitrate solution. Moroz et al. (2006) already reported the successful utilization of aluminum nitrate in pseudoboehmite synthesis [4]. According to this researcher, the pseudoboehmite obtained by aluminum nitrate shows the highest specific surface areas among the syntheses studied by the author. The aluminum nitrate solution was dripped on the ammonium hydroxide solution with constant stirring until it reaches the neutral pH. After pseudoboehmite synthesis in a glass reactor, the obtained gel of pseudoboehmite containing graphene oxide was vacuum filtered through a Büchner funnel and the product washed with deionized water. The gel was dried by freeze drying in a Terroni equipment. Finally, the gels were characterized using Differential Thermal Analysis (DTA), Thermogravimetric analysis (TG) and X-ray Diffraction (DRX).

Characterization of Pseudoboehmite

Thermal Analysis: the DTA and TG analysis were realized in a Netzsch equipment, model STA 449F3-Jupiter. The pseudoboehmite samples were heated from ambient temperature until 700 °C with 5 °C min^{-1} heating rate and 60 mL min^{-1} nitrogen flow.

The X-ray diffraction analyses were done in a diffractometer Rigaku MultiFlex with monochromator operating at 40 kV and 20 mA current. The scanning angle (2Θ) from 0° to 90°, radiation Kα from copper (λ = 1.542 Å) and scanning speed of 2° min^{-1}.

Production and Characterization of the Nanocomposite

The HIPS used U8884 (product specification) was from Unigel Chemical Industry. The mixture of 800 g of micronized polymer, 44.1 g of pseudoboehmite containing 0.48 g of graphene oxide was dried at 80 °C for 24 h. After drying, the mixture was used for injection in a Romi 65R equipment.

Characterization of the Composite

Thermal gravimetric (TG) analysis and differential thermal analysis of the nanocomposites were carried out in air at a heating rate of 20 °C min^{-1} from 20 °C to 700 °C with 60 mL min^{-1} nitrogen flow by using a STA 449F3-Jupiter instrument (Netzsch, Germany).

The SEM were realized at a JEOL microscopy, model 7800F PRIME operating with secondary electrons detector. The samples were fixed to a support with a carbon double-sided adhesive tape. The samples were not coated with gold or other metal. The fracture surface was analyzed using WDS detector.

The mechanical tests, 3-point flexural strength, were realized in a Zwick Roell Z100 equipment. The Izod impact was realized in a Tinius Olsen equipment model 892 without notch of the samples. Hardness test performed on the equipment Shore D Mitutoyo digital scale.

Tinius Olsen Extrusion plastometer—model MP993a—was used to determine the melt flow index. Heat Deflection temperature (HDT) was determined on composite samples with and without the addition of pseudoboehmite and graphene oxide, using the HDT/Vicat Softening Temperature apparatus trademark Tinius Olsen model HD94/398.

Results and Discussion

Characterization of Pseudoboehmite

The analysis of the "TG curve", Fig. 1, indicates that the sample present peaks at 104.8 °C in DTG curve, which indicates the physical-linked water loss.

The mass change around 274.1 °C in DTG curve is associated with pseudoboehmite conversion to γ-alumina. Probably the decomposition of graphene oxide is not observed due to the small amount of this material in the sample. In the DTA analysis, Fig. 2, the samples show an endothermic peak due to pseudoboehmite dehydration at 110.6 °C and other endothermic peak at 276.3 °C due to the conversion of pseudoboehmite into γ-alumina.

X-ray diffraction analysis (XRD). Figure 3 shows the XRD data for pseudoboehmite sample containing graphene oxide. The XRD data obtained are characteristic of pseudoboehmite. The most prominent peaks were indexed. The peak at approximately $2\theta = 65°$ has 2 peaks indexed (231) and (071). The characteristics peaks of graphene oxide at $2\theta = 19°$ and 26° were not observed probably due to the small amount of graphene oxide in the sample. There is only 0.48 g of graphene oxide disperse in 44.1 g of pseudoboehmite.

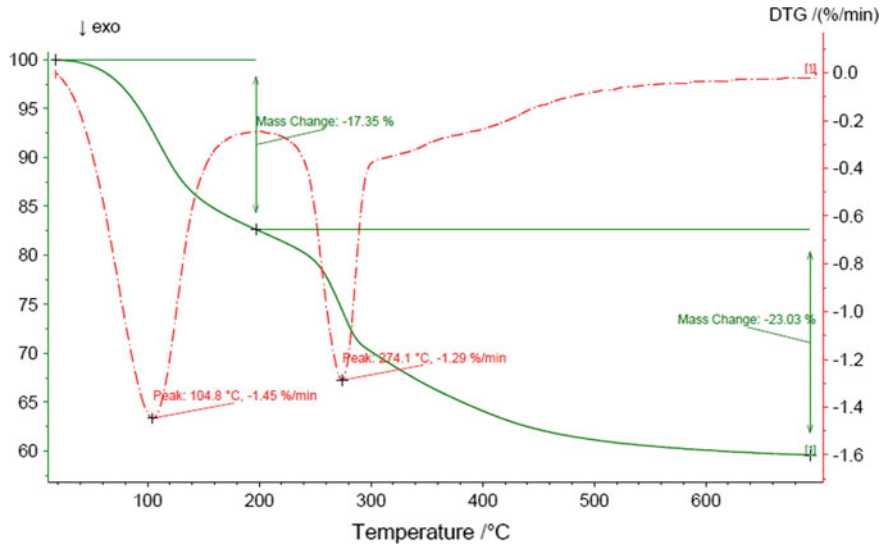

Fig. 1 TG curve of pseudoboehmite graphene oxide sample

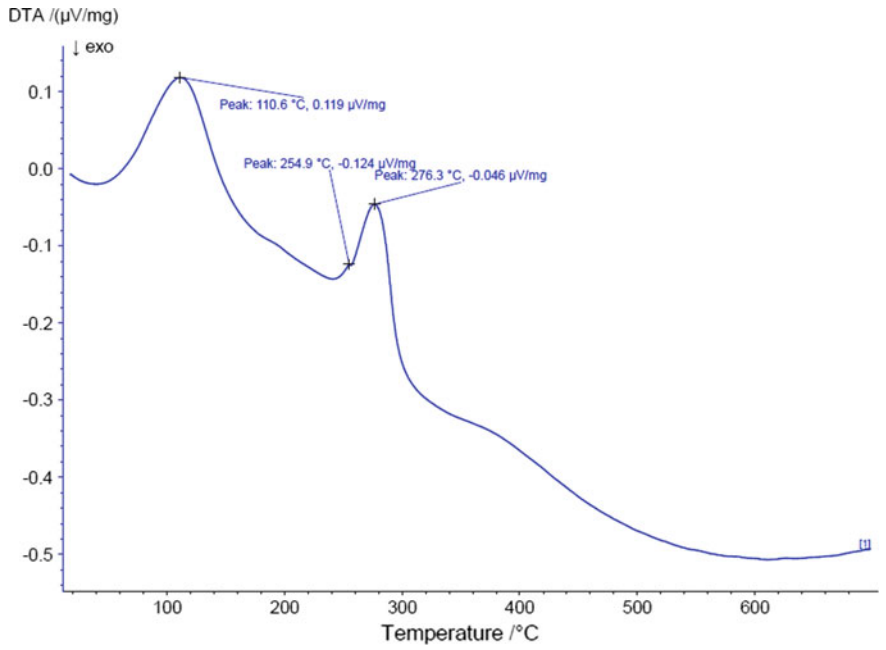

Fig. 2 DTA analysis of pseudoboehmite-graphene oxide sample

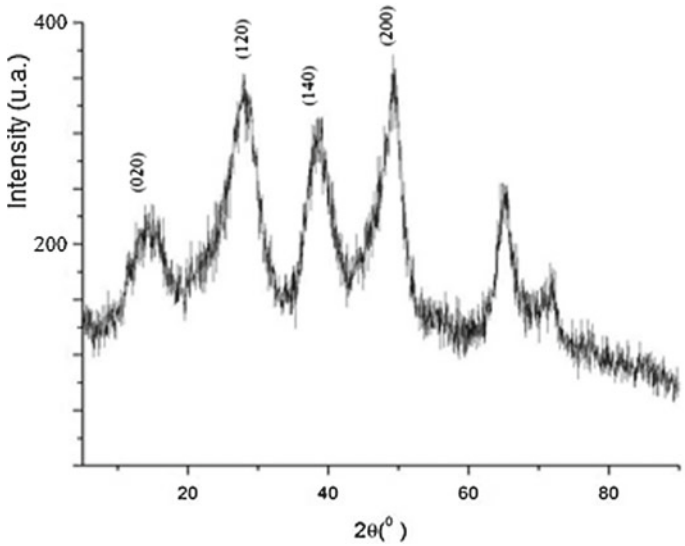

Fig. 3 X-ray diffraction of pseudoboehmite-graphene oxide sample

Characterization of the Composite

Figure 4 shows the TG curve for HIPS with and without the addition of pseudoboehmite and graphene oxide. It is observed that the mass loss begins at a low temperature for pure HIPS.

The DTA analysis shows that the melting temperature is very similar to these pure HIPS and the nanocomposite, Fig. 5a, b. Comparing the TG results for the composite and the pure HIPS, it is observed that the addition of the reinforcement resulted in a significant increase in the temperature at which the mass loss of the material begins. There is approximately 58 °C difference: 322 °C for HIPS and 380 °C for the composite. From the DTG analysis, a 19.9 °C difference is observed for the temperature at which the maximum rate of degradation is reached for the two materials; 433.1 °C for HIPS-composite and 413.2 °C for HIPS. Thermal analysis shows that the composite presented higher thermal stability than the pure HIPS.

Scanning Electron Microscopy of the (SEM): Fig. 6 shows the SEM of particles with a plate-like morphology distributed in the composite.

The analysis of the fracture region using WDS detector, Fig. 7, shows the presence of C, O, Cu, Zn and Al. The first peak at 0 keV is not associated with any element. The Al is due to the presence of pseudoboehmite. Cu and Zn are contaminants of the polymer.

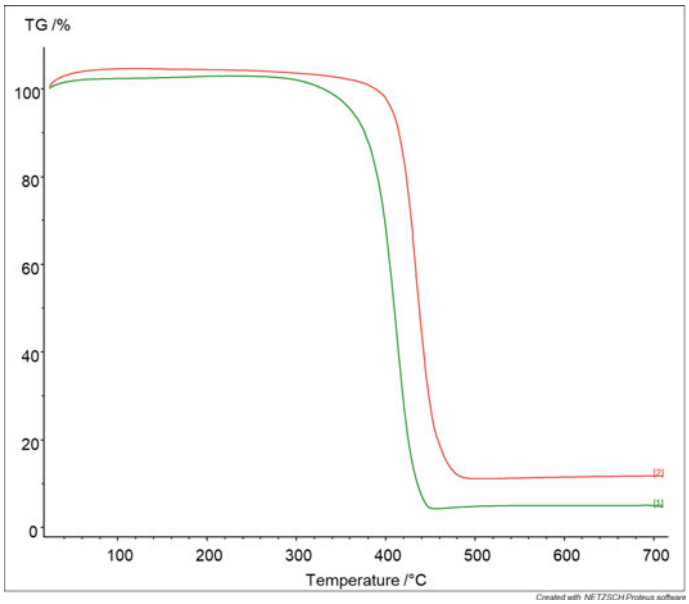

Fig. 4 TG (1) pure high-impact polystyrene (HIPS), (2) high-impact polystyrene pseudoboehmite graphene oxide composite (HIPS-composite)

Table 1 3-point flexural strength data

	HIPS			HIPS-composite		
	m	s	V (%)	m	s	V (%)
Ef (MPa)	1660	32.7	2	1848	38.7	2.1
$\delta_{0,2}$ (MPa)	22.9	2.1	9.2	32	0.6	1.9
δf_M (MPa)	34.6	1.6	4.8	37.3	0.6	1.6
εfM (%)	5.4	0.3	5.5	5.2	0.2	3.6
h (mm)	6.2	0.02	0.3	6.2	0.005	0.1
b (mm)	13.6	0.03	0.2	13.6	0.007	0.1
A (mm^2)	84	0.4	0.5	84.5	0.1	0.1

m = medium of 10 samples; s = standard deviation; V = variance; h = height of the sample; b = base of the sample; Ef = flexure modulus; $\delta_{0,2}$ = flexural stress at 0.2% plastic deformation; δf_M = flexure strength; εfM = strain at flexure strength

From the bending tests (Table 1), it is observed that the average stress supported by the HIPS-composite is higher than the pure HIPS (approximately 7.9% higher). The average deformation of the composite is lower (approximately 3.8% lower) The data shows that the composite presents greater mechanical resistance with loss of elasticity.

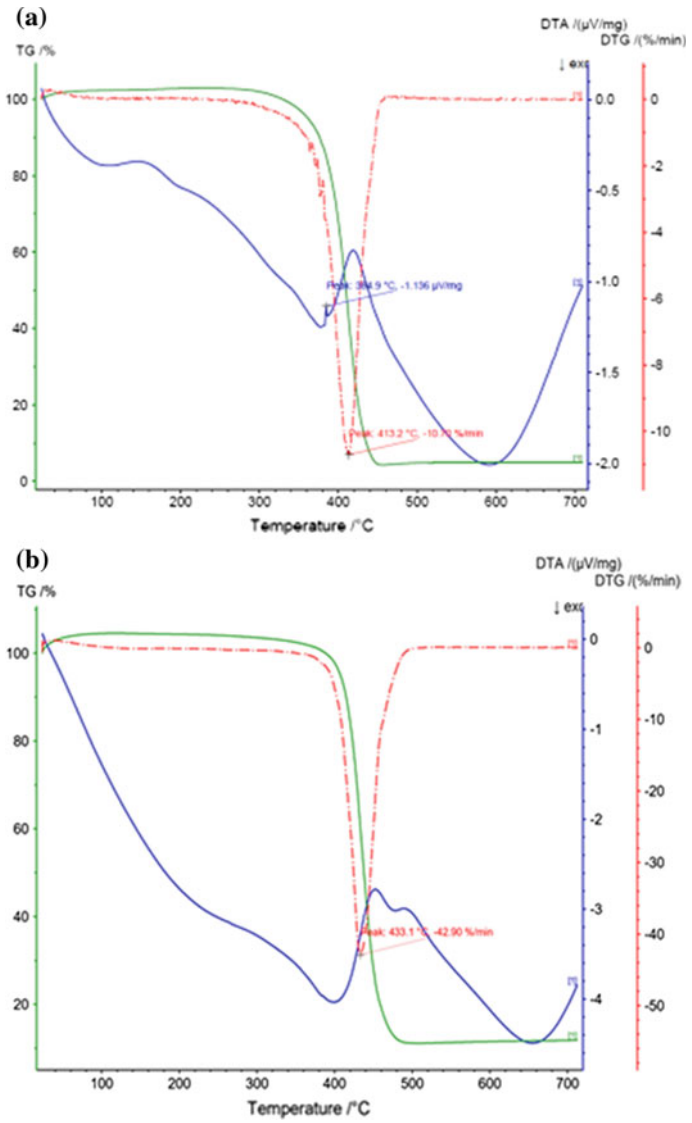

Fig. 5 TG, DTG and DTA **a** HIPS, **b** HIPS-composite

The Tensile strength data (Table 2) shows: the Elasticity modulus of the HIPS-composite is bigger than the pure HIPS. However, the deformation of the HIPS-composite is smaller than the HIPS. This shows that the addition of pseudoboehmite and graphene oxide made the material more brittle.

From the results of the Izod impact test (Table 3), it is observed the embrittlement of the composite by the addition of ceramics in its structure. The average value for

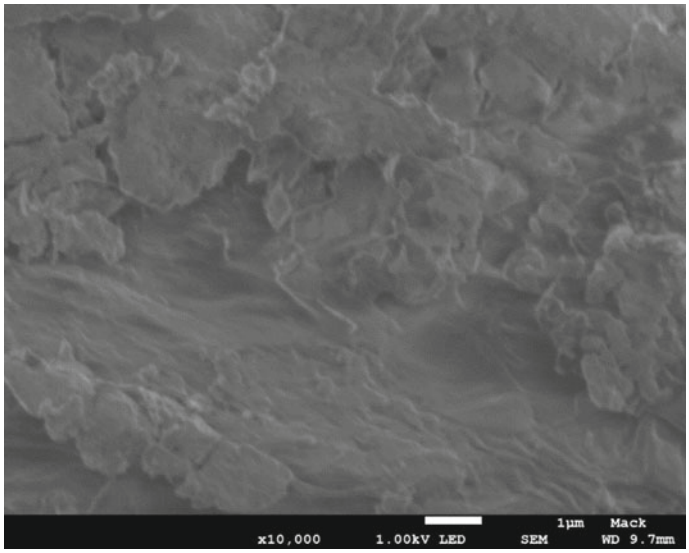

Fig. 6 SEM of the HIPS-composite

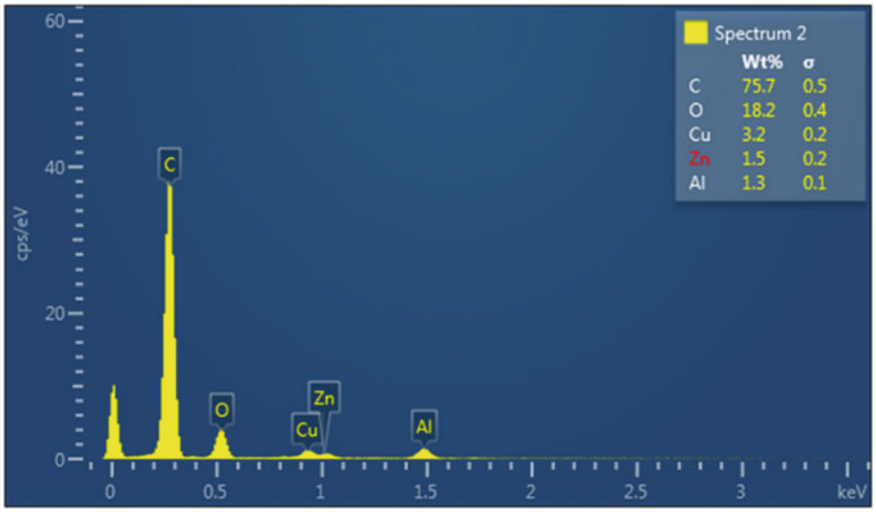

Fig. 7 WDS analysis of the HIPS-composite

the impact tests for pure high-impact polystyrene presents an energy absorbed by area by the impact considerably larger than the composite.

The data of Shore D Hardness (Table 4) shows that the addition of pseudoboehmite and graphene oxide promoted the increase in the hardness of the composite.

Table 2 Tensile strength data

	HIPS			HIPS-composite		
	m	s	V (%)	m	s	V (%)
Et (MPa)	353	72.5	20.5	387	158	40.9
Esec (MPa)	348.9	32.2	8.4	383	52.2	13.6
σ_M (MPa)	25.4	0.9	3.5	19.4	0.6	3
εM (%)	45	7.1	15.8	6.7	0.2	3.1
h (mm)	3.3	0.01	0.2	3.3	0.02	0.6
b (mm)	13.4	0.01	0.1	13.4	0.02	0.2
A (mm^2)	43.5	0.2	0.5	43.7	0.3	0.8

m = médium of 10 samples; s = standard deviation; V = variance, h = height of the sample; b = base of the sample; Et = Tensile modulus elassticity; Esec = secant modulus Elasticity; σ_M = Tensile strength; εM = elongation at Tensile strength

Table 3 Impact izod

Sample		Thickness (mm)	Length (mm)	Energy (J)	Energy F (thickness) (kJ m^{-1})	Energy F (area) (kJ m^{-2})	Impact velocity (m s^{-1})
HIPS pure	Average	3.2	14	4.16	1284.3	95.9	3.45
	Standard deviation	0.02	0.08	1.91	344.6	25.7	0
HIPS composite	Average	3.37	13.43	0.55	162.6	11.6	3.46
	Standard deviation	0.14	0.04	0.07	23	29.44	0

Table 4 Shore D results

Sample	Shore D hardness
HIPS pure	83.5
HIPS composite	88.5

The HIPS-composite presented a considerable increase in melt flow index (Table 5) compared to pure high-impact polystyrene. At T = 190 °C, there was an increase of approximately 92% in the melt flow rate and at T = 200 °C, an increase of approximately 57%, indicating improvement in the processability of the material with the addition of pseudoboehmite.

The HDT and Vicat softening temperature data (Table 6) shows a small decrease in the values with addition of pseudoboehmite and graphene oxide in the HIPS.

Table 5 Melt flow index

Samples	Load (kg)	Temperature (°C)	Melt flow index (g/10 min)
HIPS pure	5	190	1.55
HIPS composite	5	190	2.98
HIPS pure	5	200	2.73
HIPS composite	5	200	4.28

Table 6 HDT and Vicat softening temperature

Samples		HDT	VICAT
HIPS pure	Medium	91.3	104.5
	Standard deviation	0.4	0.1
HIPS-composite	Medium	90	103.7
	Standard deviation	0.3	0.2

Conclusion

From the characterization of the composite material of high-impact polystyrene reinforced with pseudoboemite and graphene oxide, it is concluded:

From its mechanical properties, it was observed an increase in the brittleness of the composite with ceramic reinforcement when compared to pure high-impact polystyrene, resulting in lower results in the impact and tensile tests and in the elasticity decrease, given lower composite indices of deformation. Despite the fragility, an increase in fracture stress was observed in the three-point flexural test. It was concluded that the material became more brittle, but there was an increase in its hardness and flexural strength.

Regarding its melt flow index, compared to pure high-impact polystyrene, the composite presented higher indices at temperatures of 190 and 200 °C. In both situations, an increase greater than 50% in the results was observed. The melt flow index is an important property for the processing of the material and its increase represents ease of processing of the material.

From the thermal analyzes, the composite samples presented higher results in comparison to pure high-impact Polystyrene, especially in the TG results, showing a considerable increase in the temperature at which the material decomposition begins (322 °C for pure high-impact polystyrene and 380 °C for the HIPS-composite). It was concluded that there was a significant improvement in the thermal stability of the composite in relation to the high-impact polystyrene, and the composite presented as a better material for thermal applications.

Thus, it is concluded that the high-impact polystyrene composite material reinforced with pseudoboehmite particles and graphene oxide is an alternative for applications in which the material will require higher hardness, abrasion resistance and thermal stability.

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