



PRODUCTION AND CHARACTERIZATION OF POLYPROPYLENE/ AL₂O₃ COMPOSITE FOR TECHNOLOGICAL APPLICATIONS IN THE DESIGN OF AUTOMOBILE PRODUCTS

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Abstract. This study investigated the effect of Al₂O₃ microparticles calcined with different particle sizes (80µm and 6µm), with and without a silane coupling agent in the proportions of 1%, 3% and 5% by mass, in the thermal and mechanical properties of polypropylene composites produced by melt intercalation techniques. The composites were characterized by Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), the mechanical properties evaluated through tensile and impact assays as per ASTM D638-10 and ASTM D256, respectively. As a result it was observed that incorporating 1% of milled alumina (6 µm) into the matrix, showed the best thermomechanical performance, including a change in the fracture behavior of the material, which went from brittle to being ductile. The good dispersion of the filler and low wettability of the particle in the matrix promoted significant gains in the toughness and thermal stability of the material.

Keywords: Polypropylene Composite, Alumina, mechanical properties, thermal properties

1. INTRODUCTION

The use of inorganic particles has become a practice in the plastics industries to improve the mechanical properties of thermoplastics, as well as distortion temperature, hardness, toughness, rigidity and shrinkage in the molding (Manias et al. Al. (2001); Thio (2002); Miao (2003); Zurderduin (2003) and Galgali (2004)). Other more recent studies, (Moritono et. al., 2010 and Bonadie, 2011) show Polypropylene (PP) as a material that catches the attention of the automobile industry due to its good performance when comparing processing *versus* cost. However, its application is still limited due to its properties of resistance and abrasion, low resistance to impact at room temperature and at low temperatures, in addition to its low hardness. As to the use of alumina as a reinforcement in polymer composites this is still scarcely discussed, but it deserves attention because of its dielectric properties, toughness and dimensional stability (Truong et. al. 2010). It is usually produced by pressing and sintering of the powder, which results in degrees of purity varying from 80 to 99.9% Auerkari (1996). The synthesis of nano and composites based on PP with inorganic particles has been extensively studied, but there are few studies that target the preparation of PP/Al₂O₃ nano or composites (Zhao and Li (2005); Akil et. al. (2006); Truong et. al. (2010); Baskaran et. al (2011)). Much of this research (Alyali 2012 and Yadava, 2012) seeks to optimize the treatment agent to modify the inorganic nanoparticle organically, or studies seeks to optimize its dispersion in the matrix of a modified PP. However, few of these studies based on PP nanocomposites have been put into practice because the melt viscosity increases with the increase in the interface area of the resin with the filler and the treatment agent needed for the treatment for the nano dispersion of the filler increases the costs of the production process (Moritono et. al., 2010).

This study investigated the effect of alumina with different particle sizes (80µm and 6µm), with and without treatment of the surface with silane, it acting as a filler in PP composites, that target product development which require good thermal stability and toughness with respect to fracture, properties required by devices that sustain mechanical elements, such as radiator supports in automobiles, while maintaining the processability characteristics of the material. The composites were characterized by Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), the mechanical properties being evaluated through tensile and impact assays as per ASTM D638-10 and ASTM D256, respectively.

2. MATERIALS AND METHOD

2.1 Materials

Polypropylene (HP550R) manufactured by Brasken (melt flow index of 25 g/10 min. (230°C) and density of 0.905 g/cm³) and calcined alumina was provided by ALCOA SA (purity of 98.26% and moisture: 3.19%). The coupling agent (3 - chloropropyl) triethoxysilane (95%), and Sigma-Aldrich and Anhydrous Toluene (99.8%) from VETEC as solvent. However, to ensure that it was 100% free of water or humidity, a procedure for drying the toluene was performed as described in Section 2.2, below.

2.2 Treatment of alumina and Preparation of the PP/Al₂O₃ composite

To reduce the size of the particle, the alumina underwent a grinding process in a ball mill or Alsing mill. A 100 g sample of alumina was ground and homogenised in the ball mill for 24 h and then modified by the silanization technique adapted from procedures described in Truong et. al., 2010.

All the Toluene used in the study underwent a drying procedure to ensure that the solvent was free from water or moisture. The toluene is poured over CaCl₂ in a 250 ml balloon and left to stand for 12 h. Filtration is done on hydrophobic cotton which is kept in a closed container. Pieces of metallic sodium (Na) are cut up and pressed, and transferred to the balloon with toluene, and the intensity of gas formation is observed. The system is kept closed with an adapter and a balloon to control the pressure. It takes The system is taken to the reflux in the distillation system for several minutes until finish the process. The reflux is stopped and benzophenone is added to the system. The appearance of the colour blue to violet indicates anhydrous toluene. In the end, the toluene is distilled and reserved in an airtight container.

In a 500 ml round bottomed balloon, 10.0 g of alumina particles was suspended in 100.0 ml of anhydrous toluene and 25.0 ml of (3 - chloropropyl) triethoxysilane (95%) was added, and the mixture refluxed for 23h at 135°C in an oil bath. Then, the suspension was transferred to centrifuge bottles of plastic and centrifuged at 5000 rpm for 5 min. After three washes in toluene, the sediment of particles was transferred to a clean glass beaker and dried under vacuum for 24 hours at room temperature. This procedure was repeated until 40 g of treated alumina was obtained in order to produce composites.

2.3 Production of the Composite

Commonly, when adding filler particles to polymers, there has been a significant loss of the filler when it is being incorporated into the matrix. Consequently the preparation of a concentrated filler improves the inclusion of the filler in the polymer (Araújo and Mélo, 2012).

When preparing concentrates (masterbatches), (80 µm and 6 µm) alumina particles were mixed at concentrations of 1%, 3% and 5% with the PP matrix and the (6 µm) alumina particles treated with silane agent were mixed at concentrations of 3% and 5% in the mixing chamber of a Haake RHEOMIX 3000 QC torque thermometer, operating at 190°C at 60 rpm for 10 minutes. The concentrates obtained, as per Table 01, were ground in a Wiley mill and mixed in the form of granules with the HP550R polypropylene matrix in the quantities necessary to obtain the desired nominal content under the same processing conditions. The identification of the samples respects the following models: A1-80 (no silane - A; proportion of alumina - 1; particle size - 80), and AS3-6 (presence of silane - AS; proportion of alumina - 3; particle size - 6) .

Table 01 – Formulation of the PP-Al₂O₃ composites .

Composite Material	Units								
	PP	A1-80	A3-80	A5-80	A1-6	A3-6	A5-6	AS3-6	AS5-6
PP	100	99	97	95	99	97	95	97	95
Al ₂ O ₃ (80µm)	0	1	3	5	0	0	0	0	0
Al ₂ O ₃ (6µm)	0	0	0	0	1	3	5	3	5
Silane Agent (S)	0	0	0	0	0	0	0	S	S

The specimens for the tensile assay (Type I - ASTM D368 10) and the impact assay (IZOD Type D - ASTM D256) were injected into a single screw injector (FLUIDMEC H30-40) with the same temperature (190°C) in both chambers. The mold temperature was maintained at 25°C, injection pressure 20%, injection flow 40%, filler 63.7 cm and cooling time 25s. The specimens used for the assays were kept under a controlled temperature of 25°C for 48 h and then subjected to mechanical tests. An average of 8 test samples for each composition was tested and the values of the properties calculated values with their respective standard deviations.

2.4 Characterization of the Composites

Thermogravimetric analysis

The TG analysis for this research was conducted using an Perkin Elmer TGA STA 6000 apparatus, under an atmosphere of N_2 at a rate of $30^\circ C$ to $900^\circ C$ and a heating rate of $20^\circ C/ min$.

Microstructural analysis

For the morphological and microstructural analysis of the samples, an Electronic Scanning Microscope JEOL (Japan), model JSM – 5900, was used. The samples were fixed to the sample holder using double sided carbon tape. Subsequently, a thin surface layer of gold was deposited by sputtering using a Metliazer, Bal SDS-tec 050 (Japan). Qualitative information about the chemical compositions of the samples were analyzed by energy dispersive spectroscopy X-ray (EDS).

Mechanical tests

The IZOD impact assay for this research was performed as per ASTM D256 - in an instrumented impact machine, model Resil 5.5, brand CEAST, pendulum of 2.75 J, friction energy 0.016 J and V-Notch with a depth of approximately 2.5 mm. As to the tensile test for evaluating the properties of the elasticity module, the ultimate tensile strength, the toughness to fracture module and elongation at rupture break was carried out at room temperature, based on ASTM D 638-10 and conducted in a mechanical assay machine EMIC DL 2000 with 20 KN, using a displacement rate of 5 mm / min. The samples for these assays, after being injected, were air-conditioned for 48 h prior to conducting the mechanical tests. An average of 8 test samples for each composition was tested and the values were calculated of the properties, with their respective standard deviations.

3. RESULTS

Thermogravimetric analysis

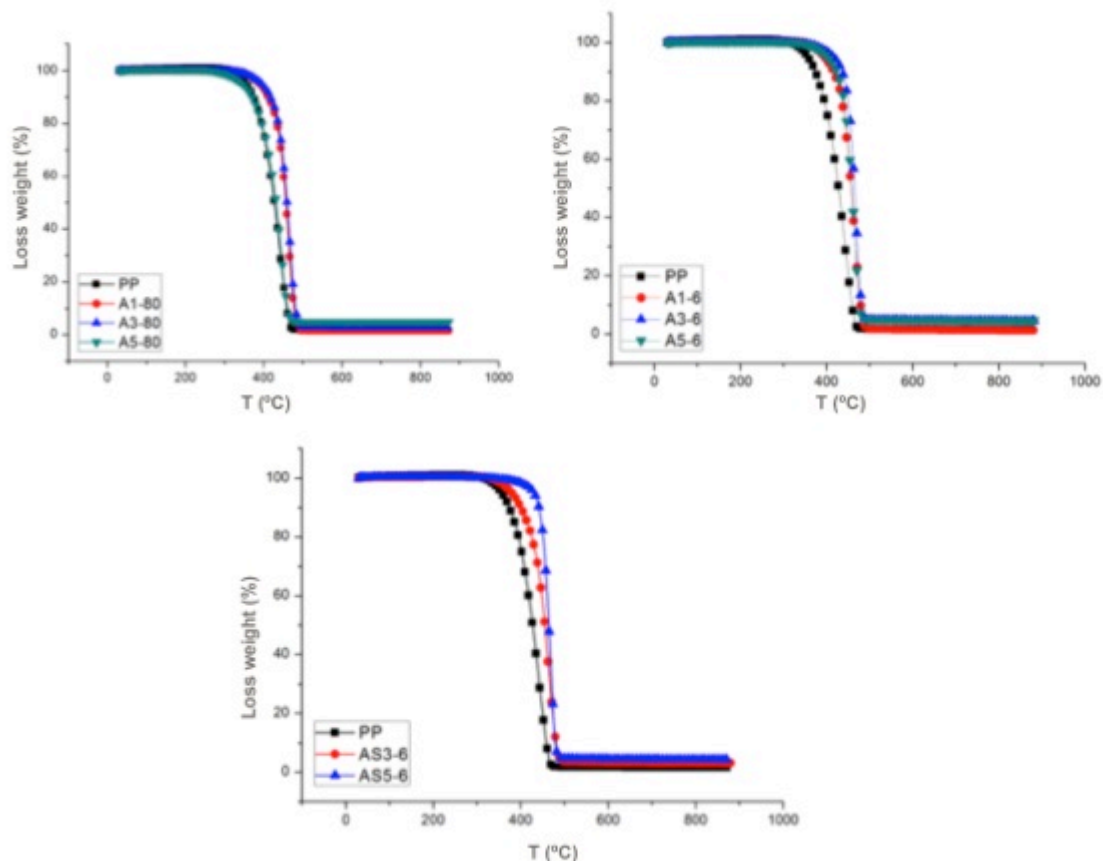


Figure 1 - TG curves for the (80 m and $6\mu m$) PP/ Al_2O_3 composites containing 1%, 3% and 5% by mass, of alumina and of the ($6\mu m$) PP/ Al_2O_3 composites containing 3% and 5% by mass, of alumina treated with silane agent.

Figure 1 shows the thermogravimetric curves (TG) of pure polypropylene and (80 μm and 6 μm) PP/ Al_2O_3 composites containing 1%, 3% and 5% by mass of alumina and (6 μm) PP/ Al_2O_3 composites containing 3% and 5% by mass of alumina treated with silane agent. The reduction of the particle size, the treatment of the surface and the increase of the volume by mass of the alumina caused substantial change in the thermal stability of the polypropylene. All samples showed improvement in the thermal stability of the material, but the best result of the TG for the PP composites incorporating Al_2O_3 was recorded for the percentage of 5% by mass of alumina treated with silane agent. There was an increase of 55 $^\circ\text{C}$ to start the decomposition of the material when compared to pure PP. This increase can be explained by the good dispersion and the increase of the surface area of the particle in the matrix.

Microstructural Analysis

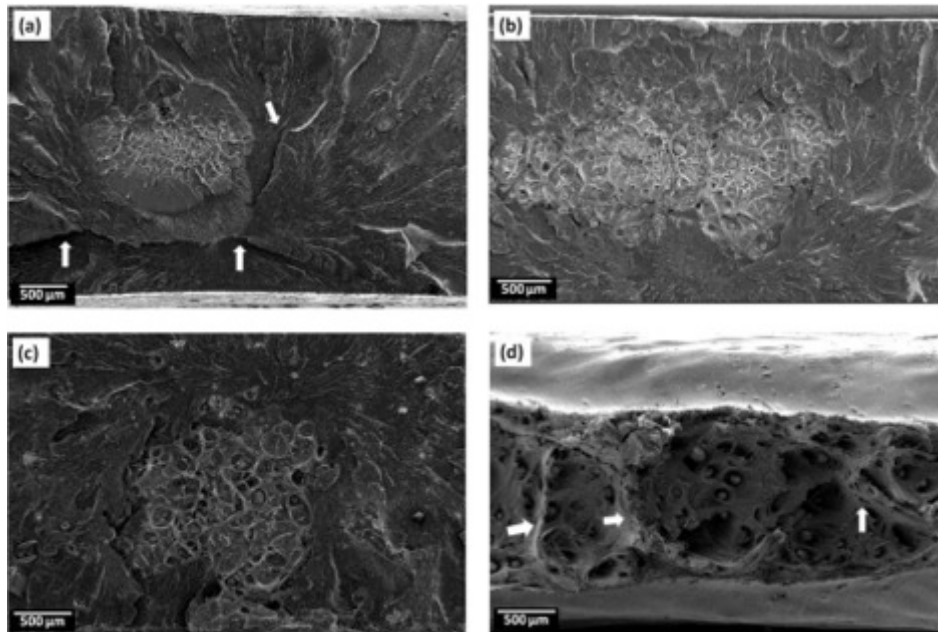


Figure 2– Micrograph obtained by SEM of the fractured surface of the pure PP (a) and the (80 μm) PP/ Al_2O_3 composites in the proportions of 1% (b), 3% (c) and 5% (d), by mass.

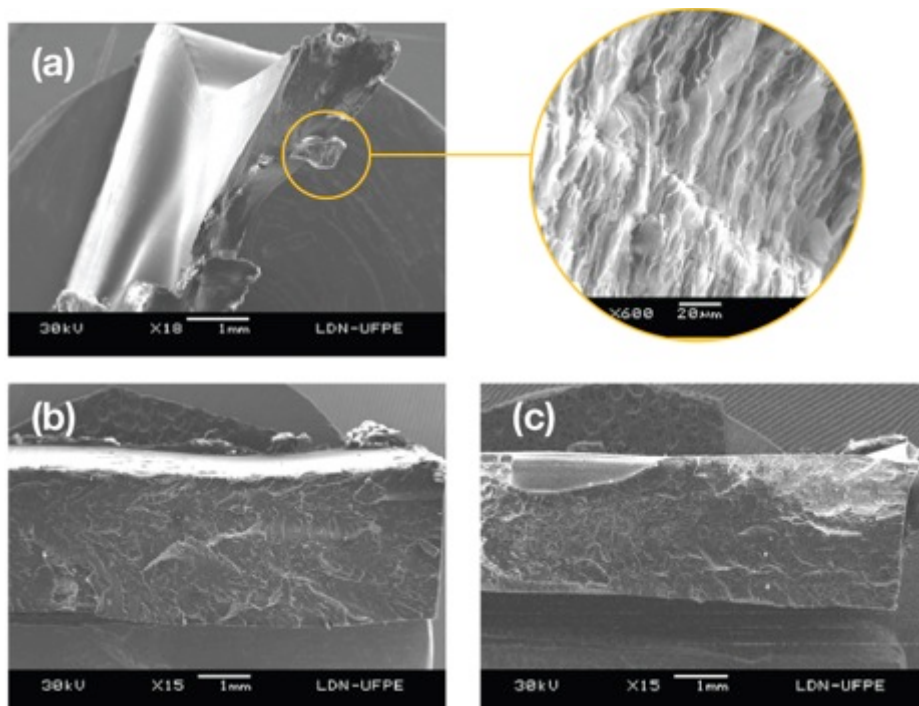


Figure 3 - SEM micrograph of the fractured surface of the (6 μm) PP/ Al_2O_3 composite in the proportions of 1% (a), 3% (b) and 5% (c), by mass.

Figure 2 shows the micrograph of the pure PP fracture and of the (80 μm) PP/ Al_2O_3 composites in the proportions of 1%, 3% and 5%, by mass. It is seen that the pure PP, Figure 2a, obtained a brittle fracture type, characterized by the flat surface and with the absence of plastic deformation. The direction of the propagation of the crack can be observed as indicated by the "arrows", these being perpendicular to the direction of traction applied. The same is true for the (80 μm) PP/ Al_2O_3 composites in the proportions of 1% and 3%, by mass. Already in the composite sample PP/ Al_2O_3 5% (80 μm) was observed ductile fracture surface with a very fibrous (Figure 2d).

Figure 3 shows a micrograph of the fracture of the (6 μm) PP/ Al_2O_3 composites in the proportions of 1%, 3% and 5%, by mass. In the sample (6 μm) PP/ Al_2O_3 composite 1%, by mass, Fig. 3a, there is a ductile fracture from a very fibrous surface. In Figures 3b and 3c there are brittle fracture types, since the direction of the propagation of the crack is perpendicular to the direction of the traction applied.

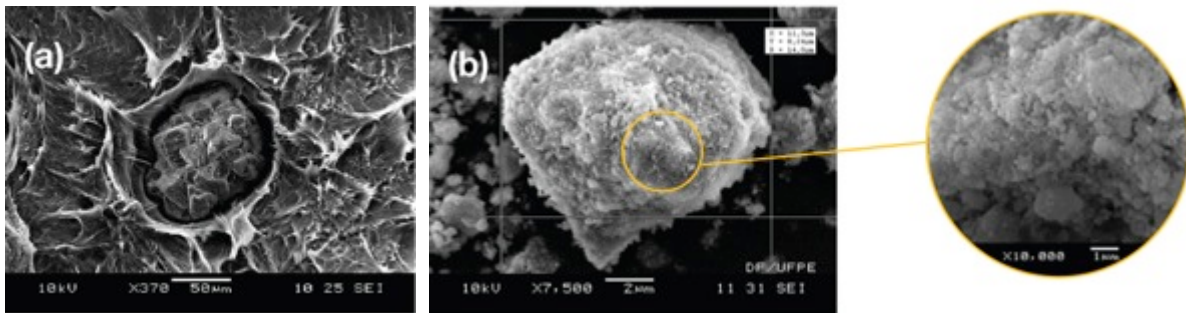


Figure 4 – Details of the micrograph of the surface of the particle before (a), and after (b) treatment with silane agent

Figure 4. shows the surface of the particle before and after the treatment with the silane agent. The detail of Figure 4b shows the surface of the alumina with a velvety aspect regarding the efficient coating of the agent in the particle. Figure 5 shows the micrograph of the fracture of the (6 μm) PP/ Al_2O_3 composites with alumina treated with silane agent in the proportions of 3% and 5%, by mass. The fracture behavior for both samples, Fig.5a and 5b, showed brittle type fractures.

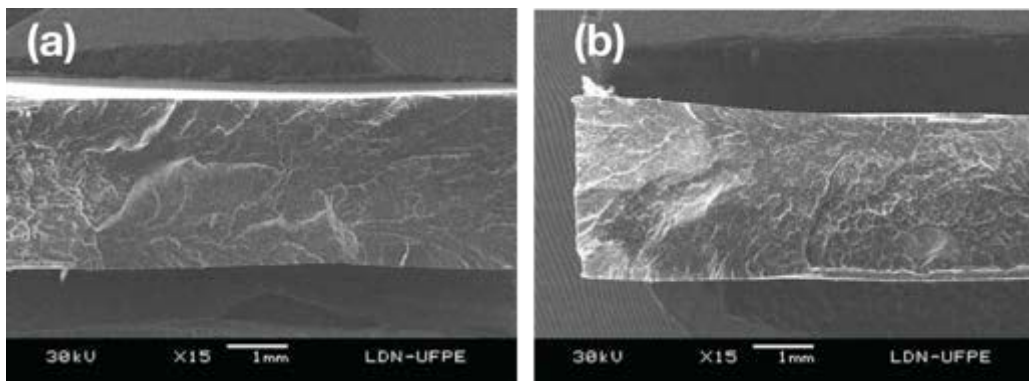


Figure 5– Micrograph obtained SEM of the fracture surface of the PP/ Al_2O_3 composite (6 microns) treated with silane agent in the proportions 3% (a) and 5% and (b) by mass

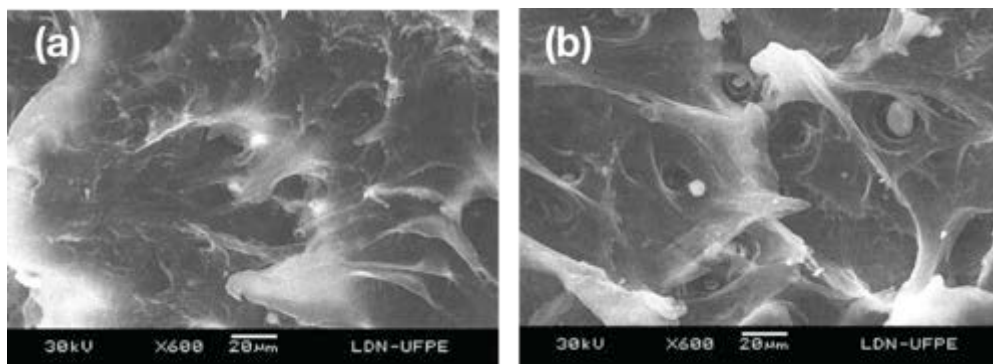


Figure 6 - Micrograph Details of the fracture surface of the PP/ Al_2O_3 composite (6 microns) treated with silane agent in the proportions 3% (a) and 5% and (b) by mass

Figure 6 shows in detail the surface of the fracture of the (6 μm) PP/ Al_2O_3 composites treated with silane agent in the proportions 3% (a) and 5% (b), by mass, with higher magnification. It can be stated that even after treating the alumina with silane agent there was no adhesion of the alumina in the polypropylene characterized by the shape of the detachment of the particle in the matrix.

Mechanical tests

Figure 7 shows the tensile versus the deformation graphs of the pure PP and (80 μm e 6 μm) PP/ Al_2O_3 composites with and without treating the surface with different levels of alumina, and from which the values of the elasticity modulus, of the limit of the tensile strength, of the toughness module and of the elongation at rupture. The values for each property measured are shown in Table 02.

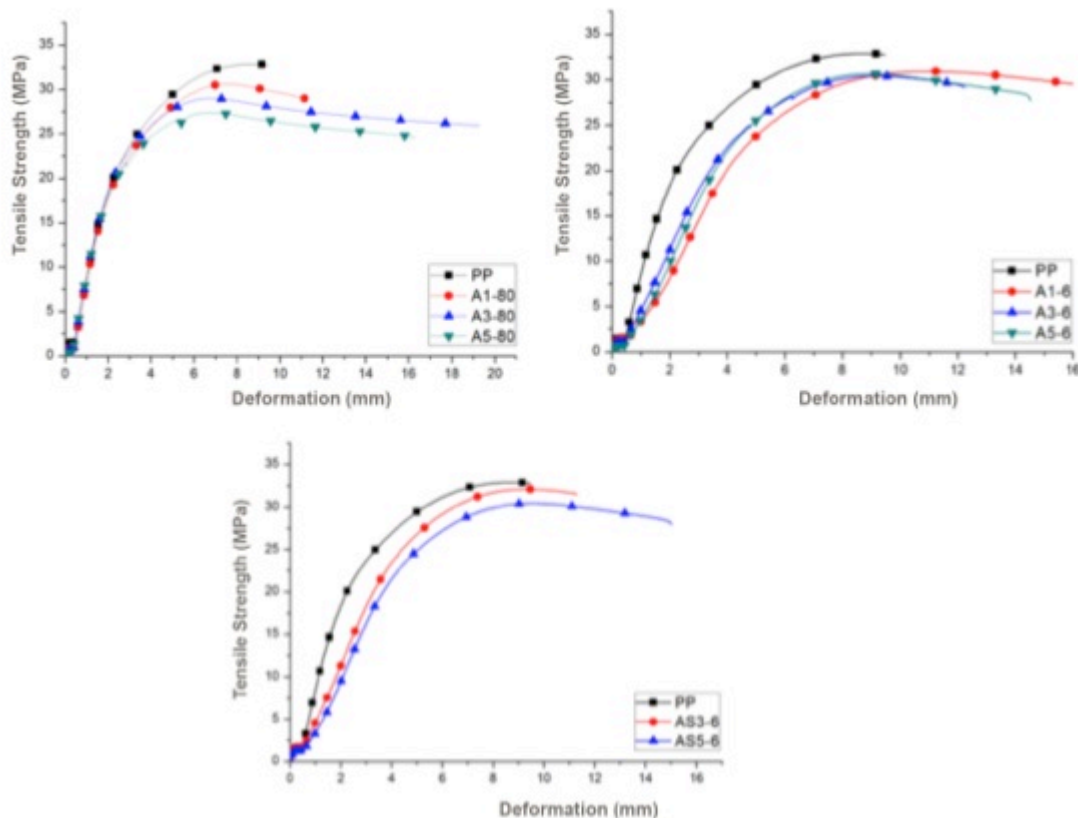


Figure 7 – Tensile *versus* deformation graph for pure PP for the (6 μm) PP/ Al_2O_3 composites with 1%, 3% and 5%, by mass, and of the composites with (6 μm) PP/ Al_2O_3 treated alumina with 3% and 5%, by mass.

Table 2– Effect of incorporating alumina into the mechanical properties of the PP- Al_2O_3 composite

Sample	Elasticity Module (MPa)	Tensile Resistance (MPa)	Toughness Module (MJ/m^3)	Total Elongation (%)
PP	1337.3 \pm 35.8	32.9 \pm 0.3	202 \pm 22	15 \pm 1
A1-80	1371.9 \pm 50.6	30.8 \pm 0.7	256 \pm 21	18 \pm 2
A3-80	1429.2 \pm 46.4	28.8 \pm 1.0	422 \pm 68	30 \pm 5
A5-80	1356.1 \pm 55.4	27.4 \pm 0.4	381 \pm 32	29 \pm 3
A1-6	643.1\pm13,2	30.4\pm0.6	472\pm53	34\pm3
A3-6	686.6 \pm 16.3	30.6 \pm 0.4	292 \pm 48	22 \pm 3
A5-6	715.3 \pm 13.5	30.8 \pm 0.3	322 \pm 46	24 \pm 3
AS3-6	717.8 \pm 17.0	31.8 \pm 0.4	258 \pm 13	20 \pm 1
AS5-6	688.7 \pm 5.0	30.5 \pm 0.3	331 \pm 59	25 \pm 3

An increase in total elongation values is observed for (80 μ m) PP/Al₂O₃ composites with 3% and 5% alumina, by mass, and for the (6 μ m) PP/Al₂O₃ composite with 1% alumina, by mass. The values of the elasticity module showed no significant changes for the incorporation of (80 μ m) alumina composites. However, there was a reduction in this property by incorporating (6 μ m) alumina particularly for composites containing alumina content of 1% and 3%, by mass. As to the tenacity and total elongation modules, they underwent significant gains with the reduction of particle size, especially for the (6 μ m) PP/Al₂O₃ composite with 1%, by mass, of alumina.

4. CONCLUSIONS

The effect of incorporating alumina with different particle sizes (80 μ m and 6 μ m), with and without treating the surface with silane, acting as filler in PP composites prepared by the melt intercalation method, targeted on developing products with requirements for good thermal stability and toughness to fracture was evaluated experimentally. The microparticle of alumina was shown to be a viable alternative as filler in commercial polypropylene HP550R for automotive applications, it being credited with gains in the values of thermal stability, of the toughness module and of total elongation. The chemical treatment of the alumina used in this study was efficient in coating the surface of the particle, but there was no increase in the wettability of the particle with the matrix which was expected as a result of the review of the literature. In this study, surface treatment with silane agent showed no significant gains in the mechanical properties of the composite, except for the thermal properties of the material. The incorporation of 1% (6 μ m) milled alumina in the PP matrix without surface treatment showed the best result from the tensile assays with significant gains in the toughness of the material.

4. ACKNOWLEDGEMENTS

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