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Macromolecular coupling agents for flame retardant materials

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Abstract

Polypropylene (PP) is a large-consumed polymer employed in many applications. For some uses, good flame resistance is desirable and this can be achieved by the addition of metallic hydroxides. However, high loads of metallic hydroxides are needed causing marked deterioration of the physical properties. Addition of interfacial agents is a useful way of minimizing these effects. In this study, PP was modified with vinyltriethoxysilane (VTES) and maleic anhydride (MA) and the products were used as coupling agents for PP/aluminum hydroxide (ATH) composites. The composites were characterized by TGA, SEM, tensile and flammability tests. It was observed that both coupling agents were efficient but PP modified with VTES showed better effect on the mechanical properties. Two types of ATH were used for comparison.

Keywords: Polymer composites; Aluminum hydroxide; Coupling agent; Morphology; Degradation

1. Introduction

PP and PP composites have been largely used in many applications mainly due to their low cost and good properties [1]. As their use grows, flammability and smoke emission problems acquire importance, mainly for applications that show fire risks as is the case of automotive components and electric or electronic devices. Addition of flame retardant compounds is a possible way to reduce this problem. Nowadays, halogenated compounds are the flame retardant additives that show the best cost/benefit relation for PP [2]. However, these compounds have been considered not friendly to the environment since they produce harmful gases during burn.

Aluminum hydroxide (ATH) is a well-known flame retardant for polymers free from halogens. It is an easily handled and relatively non-toxic material used for elastomers [3,4], termorigid resins [5] and thermoplastics [6–8]. The thermal decomposition of ATH releases water, subtracting energy from substrate, diluting the combustible present in the gas phase and thus retarding the thermal degradation of the polymer [6,9]. Moreover, its thermal degradation produces Al_2O_3, a refractory oxide that acts as a protective layer avoiding oxygen from

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feeding the fire [6]. However, high ATH concentrations are necessary for adequate flammability levels, in general higher than 50% [6,7]. As it is common under these circumstances important physical properties losses are found [9].

Good interaction between the phases is important for improving the properties of the composites. This can be achieved through several ways as, for example, by coating the filler with selected materials. The use of coupling agents (organosilanes, for example) tends to increase the tensile strength of the composites [10–12], fatty acids and their salts increase impact strength in spite of decreasing tensile strength [10]. Addition of polymeric coupling agents can also improve adhesion between filler particles and matrix thus leading to better properties [10,13–16]. In many cases, hydrophobic polyolefins are grafted or functionalized with polar molecules becoming more hydrophilic and able to interact with the polar functional groups of mineral fillers. Hornsby and Watson [10] observed that employing 10 wt.% or more of an acrylic acid functionalized PP improved the flexural strength of PP composites with magnesium hydroxide (MTH). Mai, Li and Zeng [13,14,16] also worked with PP grafted with acrylic acid as macromolecular coupling agent for PP/ATH and PP/MTH composites and observed improvements in the tensile and flexural strengths and an increase in the melt flow index. The authors suggested that the functionalized PP reacted with the metallic hydroxides by means of acid–base reactions between the carboxylic groups of the modified polymer and the hydroxyl groups of the filler surface. Polyethylenes modified with butyl acrylate, maleic anhydride, acrylic acid and epoxide molecules were employed by Seppälä and coworkers [15] as polymeric coupling agents for PE/ATH and PE/MTH composites. The authors compared the properties of such materials with PE/ATH composites containing estearic acid coated ATH. Observation of the morphology patterns showed that the polymeric coupling agents showed the best effect on improving adhesion. This interfacial action was particularly visible in the mechanical properties of the materials. Yang and coworkers [17] used a commercial silane-grafted HDPE (6 phr) as surface modifier for ATH in HDPE composites and observed a substantial increase in yield strength. Wang et al. [18] suggested that the crosslinking induced by the presence of the silane groups was responsible for the improvements in tensile strength for PE/ATH composites prepared with silane-grafted PE. In fact, the use of organosilanes as functionalizing molecules for PE is a common commercial practice searching for crosslinkable materials. However, similar trends are not found for PP that is mainly modified with maleic anhydride, acrylic acid and epoxide moieties in commercial products.

The effects of particle size and degree of agglomeration on the properties of polyolefin composites with mineral fillers have been studied by some authors [3,19–22]. Lee and coworkers observed that tensile strength strongly diminished with ATH particle sizes in EPDM composites [3]. According to these authors, bigger particles show less uniform distribution producing lower tensile strength. Miyata and coworkers [19] filled PP with four different types of MHT, having observed that the tensile strength was strongly dependent on the crystallite size of the filler, more than on the average particle size. They proposed that bigger crystallites show better dispersion in the resin thus improving its effective volume and so the mechanical properties. Cook and Harper [21] compared two magnesium hydroxide fillers of different morphology incorporated into PP. They verified that a platelet filler tended to orient parallel to the flow direction thus causing nucleation, whereas a pseudospherical filler resided isotropically within the matrix.

On the basis of previous studies performed in our laboratory dealing with silane functionalization of polyolefins [23,24] we studied in this article the usefulness of well-characterized silane-functionalized PP as coupling agents for PP/ATH composites. In this sense, results were compared to those obtained for composites coupled with the more common maleic anhydride-functionalized PP. The properties of composites prepared with two kinds of ATH were determined viewing to relate the morphology of the filler with the interfacial action of the coupling agents.

2. Experimental

Polypropylene (highly isotactic PP, Braskem SA), vinyltriethoxysilane (VTES, Silan GF56—Wacker Chemie), Maleic Anhydride (MA 98%—Produtos Quimicos Elekeiros SA), Aluminum trihydroxide (ATH V—high purity Vetec and ATH H—Hydrogard Alcoa Aluminio SA), Dicumyl peroxide (DCP—Aldrich Chemical Company) and Luperox 101 (Atofina Brasil Quimica Ltda) were employed as received. ATH particle sizes were determined with a Particle Size Analyser Cilas Laser 1180.

2.1. Coupling agents preparation

PP-VTES A and B (PP modified with VTES) were prepared in a mixer chamber Haake through radical reactions of PP with VTES initiated by DCP according to procedures already described [23]. PP-VTES C and PP-MA were prepared in an extruder Haake Rheomex PTW 16/25 through chemical reactions of PP and VTES or MA initiated by Luperox 101. The compositions of the systems prepared in the extruder were: 0.4 mol% VTES (or MA) and 0.1 wt.% peroxide with respect to the mass of polymer. The temperature profile of the extruder was set from 170 to 195 °C. Prior to the processing the polymers were impregnated with the coupling agent and the peroxide. Non-reacted molecules were removed by heating materials in an owen at low pressure. The degree of functionalization was determined by infrared spectroscopy, Rutherford Backscattering spectrometry and titration [23,25].

2.2. Composites preparation

Mixer chamber: The dry-mixed components were processed for 5 min in a mixer chamber Haake Rheomix 600p previously saturated with argon, at 170 °C, 50 rpm. The products were cut in small pieces.

Extruder: An extruder Haake Rheomex PTW 16/25 was used with the same temperature profile described for the preparation of the coupling agents. All the components were previously dry-mixed in a plastic bag with exhaustive shaking.

2.3. Characterization of the composites

Mechanical properties were analyzed through tensile tests in a Universal Testing Machine Emic DL 10000. Samples were prepared by mold compression, at 190 °C, for 2 min, at 0.7 kgf, followed by slow cooling (10 dg/min) until 80 °C. Results are the average of at least eight measures.

Cryogenic impact-fracture surfaces of composite specimens were analyzed by scanning electron microscopy (JEOL JSM 5800), at 20 keV, after sputter-coating with gold.

The thermal stability was evaluated by thermogravimetry (TA Instruments, Model 2050) of about 8 mg samples in air or nitrogen current at a heating rate of 20 °C/min up to 600 °C.

The minimum oxygen concentration to sustain burning (Limit oxygen index, LOI) was measured on specimens (120×6 mm^2, 3 mm thick) held vertically in a Polymer Laboratory System HTFA II Instrument referred to ASTM-D-2863.

UL 94 test was used to determine the flammability of 127 mm × 12.7 mm specimens held vertically and submitted to a Bunsen burner placed near its bottom. Classification was determined as a function of the persistence of combustion after successive applications of the burner and also whether burning drops were able to ignite cotton wool. Three classes can be defined: V0, V1 and V2. The first category corresponds to the highest requirements [26].

Melt flow indices were determined in a Ceast Equipment Junior, at 230 °C, with load of 2.16 kg. After keeping the sample for 300 s in the apparatus barrel, the melted was extruded through a die and the extruded bar was cut as 20 s interval. After cooling the bar was weighed for the melt index determination.

3. Results and discussion

3.1. ATH characterization

The curves of particle size distribution show similar patterns for both ATH (Fig. 1). However, the statistical analysis reveals that the mean diameter of ATH H particles is bigger than that of ATH V ones (Table 1).

The differences in the morphology can be seen in the scanning electron micrographs of the two powders in Fig. 2a and b. ATH V (Fig. 2a) is porous and roughly spherical with wide size distribution whereas ATH H (Fig. 2b) exhibits more smooth, well-defined faces even tough remaining the wide size distribution. A closer look at the micrographs suggests that ATH V presents higher surface area than ATH H.

3.2. Preparation and characterization of the polymeric coupling agents

Four different polymeric coupling agents were prepared from peroxide initiated reactions of PP with VTES or MA. Two functionalization reactions were performed in the mixer and two in the extruder. Compositions and results of degree of functionalization (F) are shown in Table 2.

The degree of functionalization of PP-VTES was determined by infrared spectroscopy analysis correlated to Rutherford back-scattering results (RBS), as described in Ref. [23]. The degree of functionali-

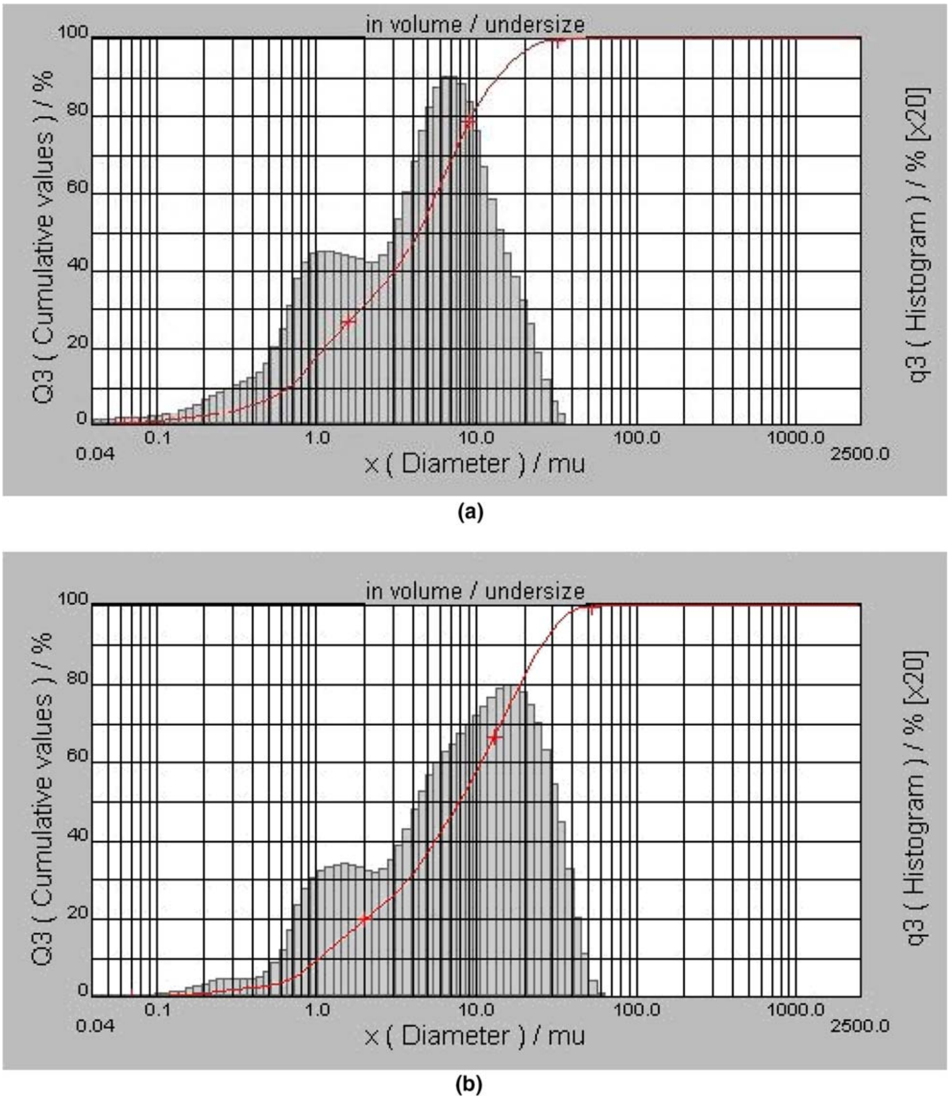


Fig. 1. Particle size distribution: (a) ATH V; (b) ATH H.

Table 1
Average particle size of ATH particles

	ATH V	ATH H
Diameter at 10% (μm)	0.66	1.04
Diameter at 50% (μm)	4.33	7.86
Diameter at 90% (μm)	13.42	25.59
Mean diameter (μm)	5.83	10.89

zation of PP-MA was determined by hydrolysis and hot titration of carboxylic groups with ethanolic KOH [25]. Functionalization reactions performed in the extruder comprised equivalent molar concentrations of VTES and MA (0.4 mol%). It was verified that the organosilane produced higher degree of functionalization, with higher conversion.

3.3. Preparation and characterization of PP/ATH composites

3.3.1. Composites prepared in the mixer

PP/ATH composites were prepared varying ATH concentration from 5 to 60 wt.% and using 3.4 or 6.8 wt.% of the interfacial agent PP-VTES.

Processability: It was observed that addition of ATH to the polymeric matrix increased the torque of the systems (Fig. 3), showing a reduction in the processability of the products as it was expected.

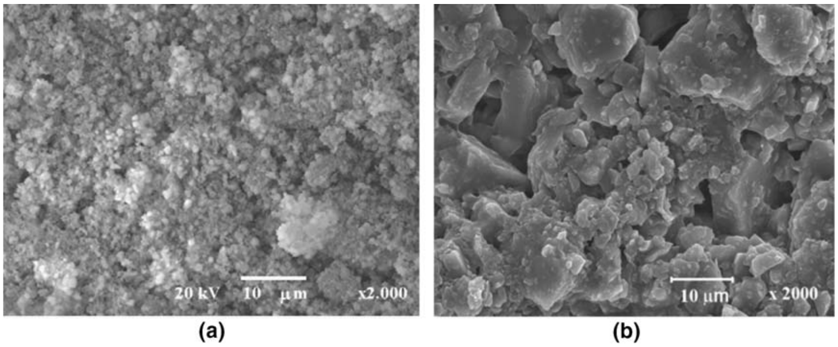


Fig. 2. SEM micrographs: (a) ATH V; (b) ATH H.

Table 2
PP functionalization

	Equipment	VTES (wt.%)	MA (wt.%)	Peroxide (wt.%)	*F* (mol%)	*F* (wt.%)	Final torque (N m)
PP-VTES A	Mixer	3.0	0	0.1[a]	0.33	1.5	0.8
PP-VTES B	Mixer	7.0	0	0.1[a]	0.98	4.4	0.8
PP-VTES C	Extruder	1.8	0	0.1[b]	0.30	1.4	–
PP-MA	Extruder	0	0.9	0.1[b]	0.13	0.3	–

[a] DCP.
[b] Luperox 101.

The presence of PP-VTES did not modify this behavior.

The melt flow indices of the products confirmed this tendency as represented in Fig. 4. Composites containing high ATH levels (more than 30 wt.%) showed very low melt flow indices and they could not be determined.

Morphology: A close look to the SEM micrographs of the composites containing 50 wt.% of ATH V (Fig. 5) allows to conclude that this filler showed good dispersion in the polymeric matrix. In this way, addition of PP-VTES did not present any visible effect on the dispersion of ATH V.

The morphology of composites prepared with ATH H was quite different. The fractured surfaces were more heterogeneous and ATH domains could be seen in SEM micrographs even for lower ATH levels (Fig. 6). This morphological characteristic can be related to the morphology of neat ATH H that has particles of bigger average size and well-defined surfaces making more difficult particle

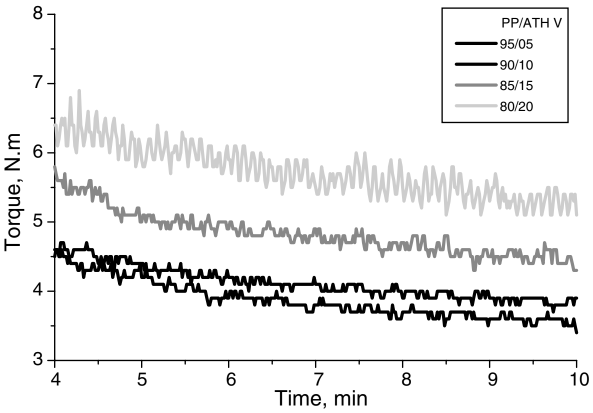


Fig. 3. Torque behavior of PP/ATH V composites.

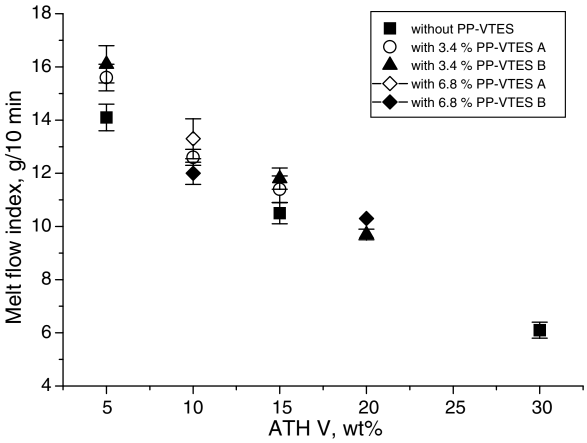
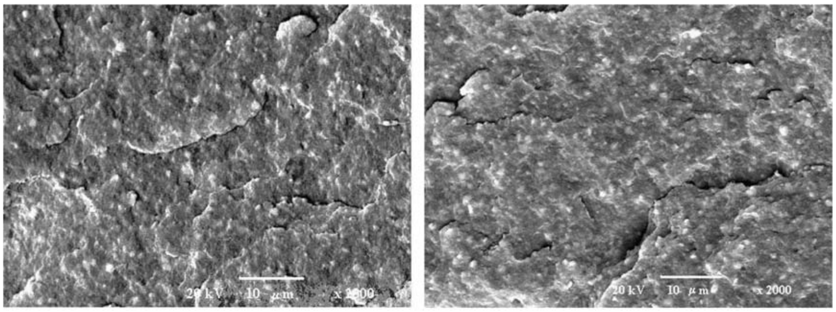
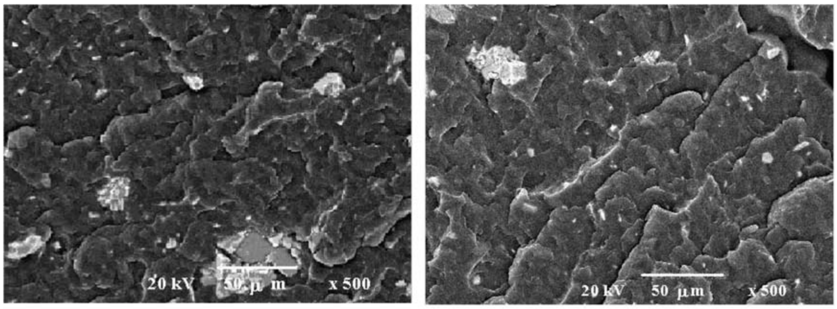


Fig. 4. Melt flow indices of PP/ATH V composites.



PP/ ATH V (50/50) PP/ATH V /PP-VTES B (46.6/50/3.4)

Fig. 5. SEM micrographs of composites containing 50 wt.% ATH V.



PP/ATH H (90/10) PP/ATH H /PP-VTES B (86.6/10/3.4)

Fig. 6. SEM micrographs of composites containing 10 wt.% ATH H.

disruption during processing. As the concentration of ATH H grew up the domains became even bigger.

Thermal degradation: Thermogravimetrical analysis were performed to investigate the composites behavior during heating under both inert and oxidative atmospheres. Shieh and Hsao [27] verified that the decomposition temperature of LDPE grafted with silane was higher than that of the virgin polymer. In that case, the authors attributed this result to crosslinking reactions due to the silane grafts. Fig. 7 shows the thermal curves of PP and PP-VTES B obtained under nitrogen. It could be seen that both materials decomposed in one step between 300 and 500 °C. In this case, we believe that crosslinking reactions did not occurred since both decomposition temperatures were similar. On the other hand, no additional degradation peak was observed that could be caused by elimination of pendant alcoxyl groups from PP-VTES.

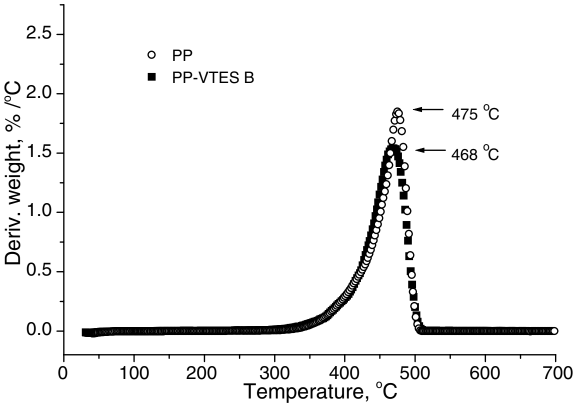


Fig. 7. DTG versus temperature curves of PP and PP-VTES B, under nitrogen.

It was observed that PP always decomposed within the same temperature range in all composites independently of PP-VTES and ATH concentration for analysis performed under nitrogen (Fig. 8). These results show that both components did not affect the degradation mechanism of PP under the employed conditions. However, a small decomposition peak was observed near 300 °C in all composites corresponding to approximately 20 wt.% of ATH concentration. This peak can be due to water elimination from ATH [28].

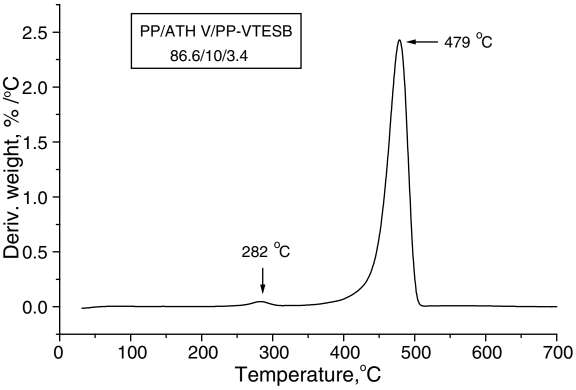


Fig. 8. DTG versus temperature curve of a PP/ATH V/PP-VTES B composite, under nitrogen.

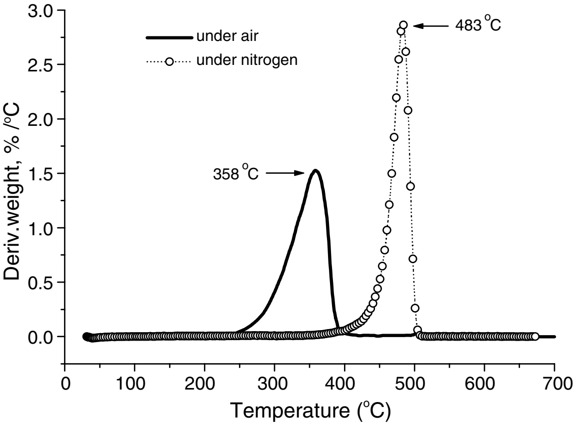


Fig. 9. DTG versus temperature curves of the composite PP/ATH V/PP-VTES B (91.6/5/3.4).

The decomposition curves of the materials were quite different under oxidative atmosphere: the virgin PP diminished its temperature of decomposition to about 320 °C while this temperature varied from 350 to 410 °C in the composites. However, in all the cases they were lower than those obtained under inert atmosphere (Fig. 9). These experimental results support the proposed mechanism for the ATH flame retardant properties: as water is released an aluminum oxide protective layer forms, preventing oxygen contact with the polymer. In this way, polymer decomposition is retarded. Once in a while some released water can disrupt the oxide layer allowing PP decomposition to occur in lower temperatures than that observed under nitrogen [28]. It was not possible to verify some effect of the presence of PP-VTES on the decomposition of the composites under these conditions.

The thermal degradation behavior of composites prepared with ATH H was similar to those prepared with ATH V.

Mechanical properties: As it was previously pointed out high ATH concentration is necessary for achieving adequate flame retardant properties in the composites. Addition of rigid particulate materials to thermoplastics tends to increase stiffness and decrease mechanical properties. Final properties are determined by size, shape, concentration and properties of the dispersed phase and by its degree of interaction with the matrix [21].

Fig. 10 shows results of tensile strength and elongation at break for the composites prepared with ATH V. In spite of the dispersion of results it was possible to observe that both properties showed a tendency to decrease with ATH concentration. Addition of PP-VTES improved the properties in most cases. These results are very important and indicate that PP-VTES can be used as an efficient polymeric coupling agent for the improvement of the mechanical properties.

Considering the dispersion of results it was not possible to conclude about the effect of using modified PP with different degree of functionalization (PP-VTES A or PP-VTES B).

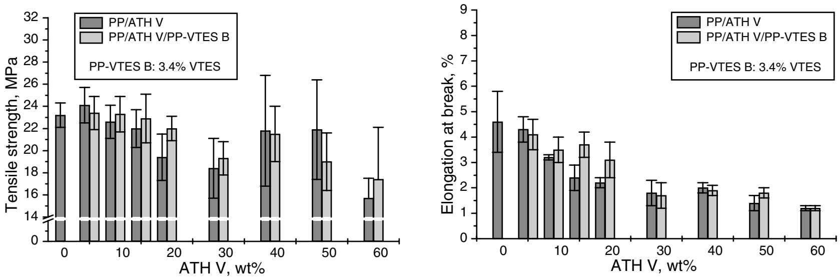


Fig. 10. Tensile properties of the composites containing ATH V (compositions from 40 to 60 wt.% ATH were submitted to higher torque during processing).

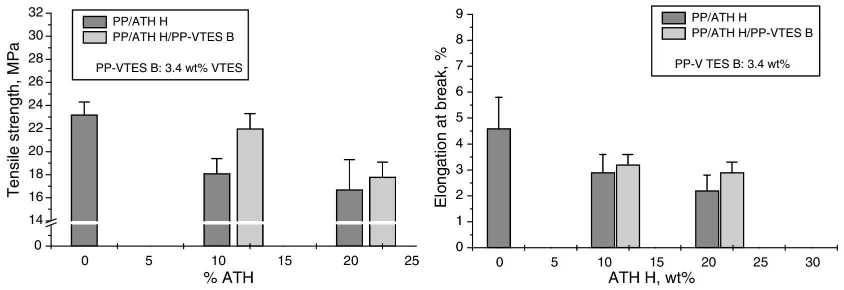


Fig. 11. Tensile properties of the composites containing ATH H.

It must be emphasized that higher amount of material was employed for the preparation of the lower-level ATH composites (up to 30 wt.% ATH) due to the equipment requirements. For high ATH concentration, the mixer requires lower mass since ATH is a less dense material. This variation in the procedure reduced the shear stress during processing of high ATH composites thus reducing the torque and improving mechanical properties.

The tensile properties of the composites containing 10 and 20 wt.% ATH H are illustrated in Fig. 11. It is possible to verify that this filler showed the worse effect on PP tensile strength as compared to ATH V. The fact can be explained by the high heterogeneity of ATH H dispersion in the polymeric matrix. On the other hand, it could be observed that the effect of PP-VTES on the mechanical properties was better for composites containing ATH H, as for example for 10 wt.% ATH composites. ATH H and ATH V composites showed similar elongation at break behavior.

Limit oxygen index (LOI) determinations and vertical flame tests (UL 94) were performed with both kinds of composites. Results are shown in Table 3. As it can be seen the minimum oxygen concentration necessary to ignite the materials (LOI) increased in all cases with respect to virgin PP and became higher as ATH concentration increased. This means that composites with higher ATH level support higher oxygen concentration before igniting.

Only the composites containing 60 wt.% ATH and also containing PP-VTES were classified as VO materials according to the UL94 tests. Some of the other compositions did not achieve this good classification because they showed flaming drops. The presence of flaming drops can be related to poor adhesion among the components of the materials. We propose that the action of PP-VTES as a coupling agent was important in promoting adhesion among the phases and helped some compositions to achieve better UL94 classification. On the other hand, it was possible to verify that composites prepared with 40–60 wt.% ATH H achieved better classification (V2 grade) than similar compositions prepared with ATH V in spite of the worse dispersion of that material in the matrix. In these cases, the after flame time criterion was carried out for all the specimens with 40 wt.% ATH or more.

Table 3
Flammability properties of the composites

PP (wt.%)	ATH V (wt.%)	ATH H (wt.%)	PP-VTES B (wt.%)	LOI (%)	UL94 classification
100.0	0	0	0	18	–
70.0	30	0	0	22	–
60.0	40	0	0	22	–
56.6	40	0	3.4	21	–
50.0	50	0	0	22	–
46.6	50	0	3.4	24	V2
40.0	60	0	0	25	V2
36.6	60	0	3.4	25	V0
60.0	0	40	0	22	V2
56.6	0	40	3.4	23	V2
50.0	0	50	0	21	V2
46.6	0	50	3.4	23	V2
40.0	0	60	0	25	V2
36.6	0	60	3.4	24	V0

3.3.2. Composites prepared in the extruder

Some composites were prepared in the extruder aiming to compare the interfacial action of PP-VTES and PP-MA. As it was previously described (Table 2) PP-VTES C showed a degree of functionalization of 0.30 mol% while PP-MA showed a degree of functionalization of 0.13 mol% nevertheless the same molar concentration of functionalizing materials was employed in the functionalization reactions. The composition of the systems and the mechanical properties of the composites are shown in Table 4.

It was observed that both PP-VTES C and PP-MA showed interfacial action since their composites

Table 4
Mechanical properties of PP/ATH H composites prepared in the extruder

ATH H (wt.%)	PP-MA (wt.%)	PP-VTES C (wt.%)	Tensile strength (MPa)	Elongation at break (%)
30	–	–	24.6 ± 1.0	5.5 ± 2.2
30	5	–	26.4 ± 1.6	5.9 ± 1.5
30	10	–	27.2 ± 2.8	3.9 ± 0.9
30	–	5	28.5 ± 2.1	4.4 ± 0.6
30	–	10	28.8 ± 1.8	4.3 ± 1.2

presented higher tensile strength than the composite without coupling agent. On the basis of the results, it was possible to conclude that PP-VTES showed higher effect on the tensile strength although variation in the concentration of PP-VTES did not significantly altered the results. Higher elongation at break was obtained when 5 wt.% PP-MA was used however this property declined for all other levels of the coupling agents.

Other experiments should be necessary to go deeper into these results. However, the adopted experimental procedure did not allow the preparation of composites with higher ATH concentrations.

4. Conclusions

The addition of ATH to PP imparts some good properties to the polymer, such as increasing decomposition temperature under oxidative atmosphere, increasing flame resistance and increasing limit oxygen concentration for ignition. However, the mechanical properties and the processability of the materials are lowered.

The morphology of the dispersed phase is important for the properties of the composites. It was verified that ATH with bigger particles showed greater deleterious effect on the tensile strength but produced better flame retardant properties.

The use of PP modified with VTES improved the tensile properties of the composites but did not modify their morphology. These results indicate that PP-VTES can be used as a macromolecular coupling agent for PP/ATH composites. The effect of this polymeric coupling agent was greater for the composites prepared with ATH of bigger particles.

By comparing PP modified with VTES and PP modified with MA it was verified that the first one showed better effect on the properties of the composites, when both were prepared with the same molar concentration of functionalizing molecules. This could be explained by the higher degree of functionalization achieved by PP-VTES in these conditions.

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References

[1] Zhang S, Horrocks AR. A review of flame retardant polypropylene fibers. Progr Polym Sci 2003;28:1517–38.

[2] Kwack SB, Nam JD. Thermo-oxidative stability of polypropylene composites by using cone calorimetry and thermogravimetry. Polym Eng Sci 2002;42(8):1674–85.

[3] Lee CH, Kim SW. Effects of particle size of $Al(OH)_3$ on electrical properties of EPDM compounds. Polym Eng Sci 2000;40(4):857–62.

[4] Pinto UA, Visconte LLY, Nunes RCR. Flame retardancy in thermoplastic polyurethane elastomers (TPU) with mica and aluminum trihydrate (ATH). Polym Degrad Stab 2000;69: 257–60.

[5] Jang J, Chung H, Kim M, Kim S, Sung H. The effect of flame retardants on the flammability and mechanical properties of paper-sludge/phenolic composite. Polym Test 2000;19(3):269–79.

[6] Yeh JT, Yang HM, Huang SS. Combustion of polyethylene filled with metallic hydroxides and crosslinkable polyethylene. Polym Degrad Stab 1995;50:229–34.

[7] Dubois PH, Alexandre M, Hindryckx F, Jerome R. Polyolefin-based composites by polymerization-filling technique. J Macromol Sci—Rev Macromol Chem Phys 1998;C38(3): 511–65.

[8] De Cirico A, Armanini M, Chini P, Cioccolo G, Provasoli F, Audisio G. Flame retardants for polypropylene based on lignin. Polym Degrad Stab 2003;79:139–45.

[9] Gallo JB, Agnelli JAM. Aspectos do comportamento de polímeros em condições de incêndio. Polímeros: Ciência e Tecnologia 1998;VIII:23–37.

[10] Hornsby PR, Watson CL. Interfacial modification of PP composites filled with magnesium hydroxide. J Mater Sci 1995;30:5347–57.

[11] Liauw CM, Lees GC, Hurst SJ, Rothon RN, Ali S. Effect of silane-based filler surface treatment formulation on the interfacial properties of impact modified polypropylene/magnesium hydroxide composites. Compos Part A: Appl Sci Manuf 1998;29(9–10):1313–8.

[12] Liauw CM, Lees GC, Hurst SJ, Rothon RN, Dobson DC. The effect of filler surface modification on the mechanical properties of aluminum hydroxide filled polypropylene. Plast Rub Compos Process Appl 1995;24(5):249–60.

[13] Mai K, Li Z, Qiu Y, Zeng H. Physical and mechanical properties of ATH/PP composites modified by in situ-functionalized PP. J Appl Polym Sci 2002;83:2850–7.

[14] Mai K, Li Z, Qiu Y, Zeng H. Interfacial interaction in ATH/PP composites modified by in situ-functionalized PP. J Appl Polym Sci 2002;84:110–20.

[15] Hippi U, Mantilla J, Korhonen M, Seppälä J. Compatibilization of PE/ATH and PE/MH composites with functionalized polyethylenes. Polymer 2003;44:1193–201.

[16] Mai K, Qiu Y, Lin Z. Mechanical properties of $Mg(OH)_2$/PP composites modified by functionalized PP. J Appl Polym Sci 2003;88:2139–47.

[17] Yang J, Zhang Y, Zhang Y. Mechanical properties and microstructure of HDPE/$Al(OH)_3$/Silicone oil composite. J Appl Polym Sci 2002;83:1896–903.

[18] Wang GL, Jiang PK, Zhu ZK. Interface modification and characterization in linear low density polyethylene highly loaded with aluminum hydroxide. Polym Compos 2002; 23(5):691–6.

[19] Miyata S, Imahashi T, Anabuki H. Fire-retarding polypropylene with magnesium hydroxide. J Appl Polym Sci 1980; 25:415–25.

[20] Velasco JI, Morhain C, Martinez AB, Rodrigues-Pérez MA, de Saja JA. The effect of filler type, morphology and coating on the anisotropy and microstructure heterogeneity of injection-moulded discs of polypropylene filled with aluminium and magnesium hydroxides. Part 2. Thermal and dynamic mechanical properties. Polymer 2002;43:6813–9.

[21] Cook M, Harper JF. The influence of magnesium hydroxide morphology on the crystallinity and properties of filled polypropylene. Adv Polym Technol 1998;17(1):53–62.

[22] Joseph R, Tanner KE. Effect of morphological features and surface area of hydroxyapatite on the fatigue behavior of hydroxyapatite–polyethylene composites. Biomacromolecules 2005;6:1021–6.

[23] Nachtigall SMB, Felix AHO, Stedile FC, Mauler RS. Polypropylene functionalization with vinyltriethoxysilane. J Appl Polym Sci 1999;72:1313–9.

[24] Nachtigall SMB, Fabris FW, Mauler RS, Stedile FC. Free-radical modification of LDPE with vinyltriethoxysilane. Eur Polym J 2004;40(6):1119–26.

[25] Nachtigall SMB, Baumhardt-Neto R, Mauler RS. A factorial design applied to polypropylene functionalization with maleic anhydride. Polym Eng Sci 1999;39(4):630–7.

[26] Toure B, Cuesta JML, Gaudon P, Benhassaine A, Crespy A. Fire resistance and mechanical properties of a huntite/hydromagnesite/antimony trioxide/decabromodiphenyl oxide filled PP-PE copolymer. Polym Degrad Stab 1996;53: 371–9.

[27] Shieh YT, Hsao KI. Thermal properties of silane-grafted water-crosslinked polyethylene. J Appl Polym Sci 1998;70: 1075–82.

[28] Hull R, Price D, Liu Y, Wills CL, Brady J. An investigation into the decomposition and burning behaviour of ethylene–vinyl acetate copolymer nanocomposite materials. Polym Degrad Stab 2003;82:365–71.