

Effect of a Macromolecular Coupling Agent on the Properties of Aluminum Hydroxide/PP Composites

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ABSTRACT: Polypropylene (PP)/aluminum hydroxide (ATH) composites were prepared in a melt mixer with addition of polypropylene functionalized with vinyltriethoxysilane (VTES) as a coupling agent. The effects of ATH and PP-VTES on the melt flow indices (MFI), tensile properties, decomposition temperatures, and flame retardancy of composites were analyzed. It was verified that increased ATH concentration reduced MFI and tensile properties, but increased the decomposition temperature under oxidative atmosphere and improved the flammability properties. Addi-

tion of PP modified with VTES slightly improved tensile strength and maximum elongation and granted the best results for the flammability tests of the materials showing that it can be an effective coupling agent for PP/ATH composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1799–1805, 2006

Key words: poly(propylene) (PP); composites; flame retardant; functionalization of polymers; degradation

INTRODUCTION

Polypropylene composites have been largely used in many applications such as in automobiles, electric and electronic pieces, furniture, and construction materials, etc. As their use increases, flammability and smoke emission features acquire great importance: addition of appropriate fire retardants and fillers can improve their fire and smoke resistance. Currently, halogenated compounds are the most efficient and cost-effective fire retardants for PP.¹ However, these compounds have not been considered friendly to the environment mainly because of the gases produced during their combustion. On the other hand, aluminum hydroxide (ATH) has also been known as an effective flame retardant filler for polymers, which is free from halogens² apart from being easily handled and relatively nontoxic.

ATH has been used as a flame retardant in elastomers,^{3,4} thermosetting resins,⁵ and thermoplastics.^{6–8} Usually, flame retardants act by delaying ignition or, after ignition, by depriving the fire of fuel or by lowering the temperature to below burning point. The endothermic decomposition of ATH, with release of water vapor, is thought to withdraw heat from the

substrate and dilute the fuel supply present in the gas phase, hence retarding the rate of thermal degradation.⁶ Further on, it produces the refractory oxide A_2O_3 that acts like a protecting layer on the substrate surface, preventing oxygen from feeding the fire. This stable product not only insulates the substrate, but also can reduce the amount of carbon entering the flame, playing a significant role in the smoke-suppression mechanism. However, to achieve the required flame retardancy, high loads of ATH are needed, usually higher than 50%.^{6,9,10} Under these circumstances, as it is common for most other inorganic fillers, there is a marked deterioration of the physical properties of the material.

The surface modification of fillers is known to be an interesting way to improve interfacial adhesion among the components of polyolefin composites⁷ in such a way that their properties are enhanced. Hornsby and Watson¹¹ studied the mechanical behavior of PP composites containing metallic hydroxides treated with magnesium stearate. They observed that mechanical properties were strongly affected by the chemical nature and amount of surface coating.

Improved adhesion among filler particles and matrix can also be achieved by the use of polymeric coupling agents. May et al.^{10,12} have investigated the effect of acrylic acid-grafted PP on ATH/PP composites properties, and verified that better interaction between the components caused an increase in the melt-flow index, and improved the tensile and flexural

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strength. However, the impact strengths were lower than those obtained for the unmodified composite ones.

Seppälä and coworkers⁹ have used functionalized polyethylene and stearic acid as coupling agents for polyethylene/ATH composites. Morphology patterns indicated that only the polymeric couplers improved the adhesion. The coupling effect was particularly reflected in the mechanical properties. Ethylene-propylene rubber, functionalized with maleic anhydride, has been used by some researchers^{13,14} as a polymeric coupling agent for PP composites with metallic hydroxides. In these cases, they have observed improvement in toughness; similar PP composites, having filler treated with magnesium stearate, showed higher matrix rubber dispersion, leading to a further increase in impact strength. Liauw et al.¹⁴ proposed that the encapsulation of the filler particles by the crosslinked elastomeric phase afforded a better balance between strength and toughness for impact-modified polyolefin/metallic hydroxide composites.

Wang et al.¹³ observed that silane-crosslinked polyethylene has inhibited combustion and smoke emission in polyethylene/metallic hydroxide compounds. It was suggested that the crosslinked polyethylene was responsible for the improvement of the properties.

The study described in this article is related to the investigation of the coupling effect of PP modified with vinyltriethoxysilane (PP-VTES) in PP composites with ATH.

EXPERIMENTAL

Materials

Isotactic polypropylene (Braskem SA), free from additives, vinyltriethoxysilane (Silan GF56, Wacker Chemie), dicumyl peroxide (Aldrich Chemical Company, Milwaukee, WI), and aluminum trihydroxide (Vetec) were used as received.

Polymer modification and composite preparation

Functionalized polymers and composites were prepared in the mixer chamber of a Haake 600p, previously saturated with argon, operating at 50 rpm for 10 min, at 170°C.

Characterization

ATH

A scanning electron microscope Jeol JSM 5800 operating at an voltage of 20 keV was used to examine the ATH, which was glued on a SEM stub and coated with gold. A Cilas Laser particle size analyzer, model 1180, was employed for ATH particles sizes analyses.

PP-VTES

The modified PP obtained in the mixer was cut in small pieces and submitted to low pressure at 60°C, for 20 h, aiming at the elimination of unreacted silane. Films were prepared at 170°C, under 5000 kgf, for 1 min, in a Carver press. These films were analyzed by FTIR using a Bomem MB 102 spectrometer. The Si—O—C absorption area of the silane groups around 1100 cm⁻¹ was related to C—H bending absorption of PP at 899 cm⁻¹. These ratios were related to the absolute degrees of functionalization (F) determined by Rutherford backscattering spectrometry analysis, according to the equation $F \text{ (wt \%)} = 0.31 \times [(A_{1100}/A_{899}) - 0.8]$.¹⁵ Conversion was calculated relating F with the amount of employed VTES.

PP/ATH composites

The mechanical properties were evaluated by tensile tests conducted on an Emic DL 10,000 instrument, at crosshead speeds of 10 mm/min. Tensile specimens were prepared by hot-compression molding at 190°C and 700 kgf, for 2 min, and then cooled to 80°C at the rate of 10°C/min. Reported results are an average of at least eight tests. Cryogenic impact-fracture surfaces of the composite specimens were analyzed by SEM after sputter-coating with gold.

Thermal stability was evaluated by TGA (TA Instruments, model 2050, around 8 mg) in air or nitrogen current at a heating rate of 20°C/min up to 1000°C.

The minimum oxygen concentration (limiting oxygen index, LOI) required to sustain burning was measured on specimens (120 × 6 mm², 3 mm thick) held vertically in a polymer laboratory system HTFA II instrument, using ASTM-D 2863.

The UL 94 test was used to determine the flammability of 127 × 12.7 mm² 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.¹⁶

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

RESULTS AND DISCUSSION

PP functionalization reactions and characterization of products

The PP functionalization reactions were carried out using 1.0–7.0 wt % vinyltriethoxysilane (VTES) and

TABLE I
Melt Functionalization of PP with VTES

VTES (wt %)	DCP (wt %)	F (wt %)	Conversion (%)	Final torque (Nm)
4.0	0	1.2	30	1.9
5.0	0	1.1	22	1.7
1.0	0.10	0.6	60	0.9
3.0	0.10	1.5 ^a	50	0.8
4.0	0.10	2.2	55	0.7
5.0	0.10	2.5	50	0.4
7.0	0.10	4.4 ^b	63	0.8
5.0	0.30	2.8	56	0.3
5.0	0.50	3.0	60	0.2
5.0	0.75	3.6	72	0.1
5.0	1.00	3.4	68	0.1

^a PP-VTES A.

^b PP-VTES B.

Mixing conditions: 170°C, 50 rpm, 10 min.

F, Degree of functionalization.

Conversion, (VTES incorporated/VTES employed) × 100.

0.1–1.0 wt % dicumyl peroxide (DCP) with respect to PP amount. Two reactions were carried out without peroxide to see the efficiency of the systems on silane incorporation. Table I shows the VTES and DCP relative concentrations, the functionalization degree F, conversion and final torque of the systems.

It was observed that PP and VTES showed good reactivity. Even in the absence of peroxide, an appreciable amount of VTES was incorporated into the PP chains showing 22–30% of conversion. Conversion was always greater than 50% in the presence of peroxide.

The degree of functionalization of PP increased with VTES concentration. A linear relation was observed between the degree of functionalization (F) and the VTES concentration, when the peroxide amount was equal 0.1 wt %, as shown in Figure 1. In general, increasing DCP concentration increased the degree of functionalization.

The processability of the products was analyzed through torque measurements during mixing. Torque reduction was observed with peroxide concentration increasing, indicating the occurrence of chain scission reactions that are very common in PP radical reactions.¹⁷ No detectable gel content was found in PP-VTES boiling xylene solution.

Two modified PPs were employed as coupling agents for PP/ATH composites: modified PP containing 1.5 wt % of VTES, named PP-VTES A, and modified PP containing 4.4 wt % of VTES, named PP-VTES B. Both showed the same final torque in the preparation reactions, indicating similar processability.

PP/Aluminum hydroxide composites

Aluminum hydroxide (ATH) was analyzed with respect to its morphology and particle size distribution.

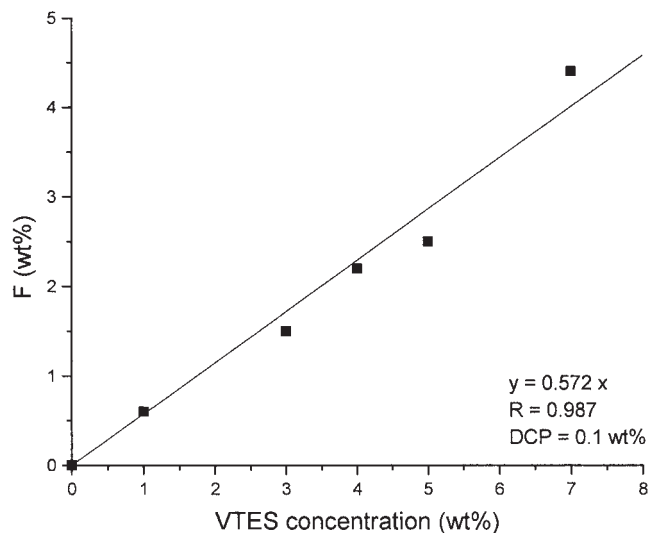


Figure 1 Degree of functionalization (F) versus VTES concentration.

Figure 2 shows the micro structure of ATH where it is possible to see that small rounded grains form agglomerates of irregular shapes and widely distributed sizes. This was confirmed through laser diffraction analysis, which displayed a bimodal particle size distribution curve (Fig. 3) with mean value 5.83 μm .

The binary PP/ATH and ternary PP/ATH/PP-VTES composites were prepared varying the ATH concentration from 5 to 60 wt %. It was observed that addition of ATH to the polymer matrix increased the torque of the mixture, as can be seen in Figure 4, reducing the PP processability. Similar results were observed for corresponding compositions containing PP modified with VTES.

The lower processability of the PP/ATH composites was confirmed by their melt flow indices that decreased with the increasing of ATH amount from

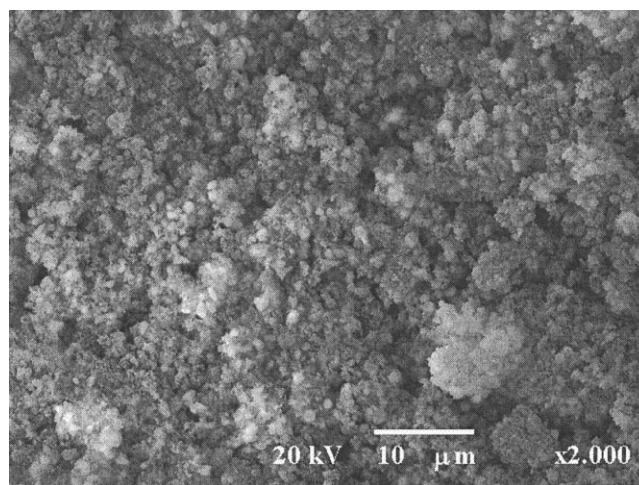


Figure 2 SEM micrograph of ATH.

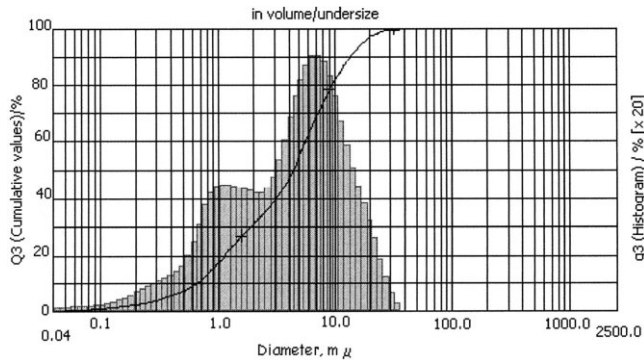


Figure 3 Particle size distribution of ATH determined by laser diffraction.

around 16 g/10 min to 6 g/10 min (Fig. 5). This was a consequence of the undeformability of the filler in the material and its lack of contribution to the flow. The melt flow index of the virgin PP was about 15.4 g/10 min. Melt flow indices of compositions with ATH content higher than 50 wt % could not be determined.

In spite of the poor processability of the PP/ATH composites, SEM micrographs of the binary and ternary composites showed that ATH was uniformly dispersed in the polymer matrix as illustrated in Figures 6 and 7. As the mean diameter of neat ATH agglomerates was around 5.8 μm , it was observed that these agglomerates underwent disruption when subjected to mechanical constraints during processing. Samples with high ATH content showed a number of bigger particles dispersed in the PP matrix (Fig. 8).

As it is known, ATH is an effective flame retardant for polyolefins, nevertheless high loadings are required before any significant effect is achieved. Incorporation of rigid particulate material to thermoplastics gives rise to enhanced stiffness and deleterious mechanical properties. Final properties not only depend

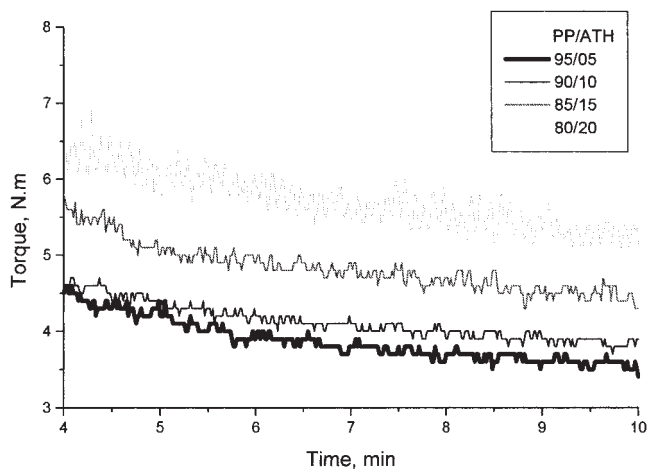


Figure 4 Torque behavior of PP/ATH composites.

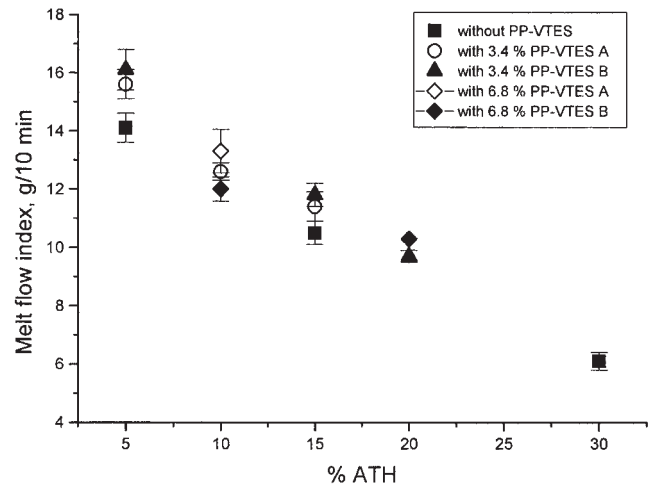


Figure 5 Melt flow indices of composites.

on the particles size, shape, and concentration but also on additive properties. Furthermore, the interaction between the filler and the matrix must be considered for good results.^{13,18}

Tensile strength and maximum elongation of PP/ATH composites, with or without PP-VTES, were evaluated to study the ATH loading effect on the final properties. Figures 9 and 10 show the variation of the tensile strength and maximum elongation, respectively, with the increase of ATH in the composites. Because of the equipment limitations, samples prepared with 40–60 wt % ATH comprised a lower mass in the mixer chamber than those prepared with up to 30 wt % ATH. Because of this, composites with higher ATH content were submitted to lower mechanical stress during processing. As a consequence, less chain scission reactions occurred^{17,19} and mechanical properties increased

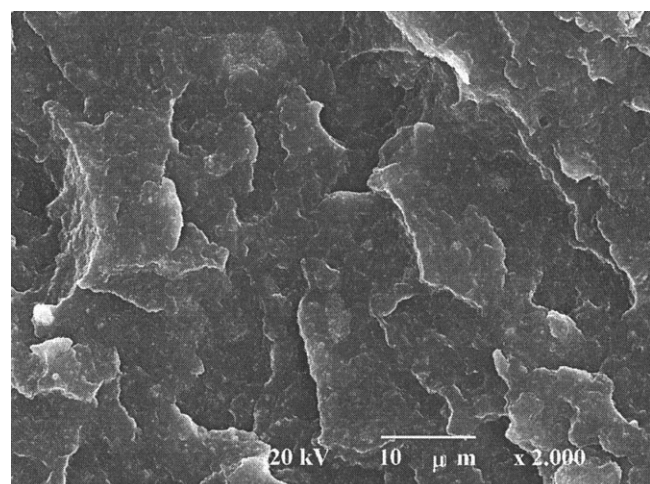


Figure 6 SEM micrograph of the composite PP/ATH (80/20).

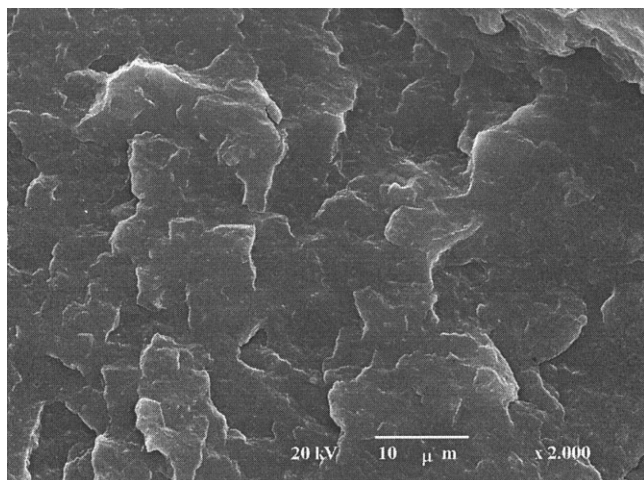


Figure 7 SEM micrograph of the composite PP/ATH/PP-VTES B (86.6/10/3.4).

with respect to the systems with 0–30 wt % ATH. Despite the high standard deviation of results, it is possible to verify that the properties of the composites slow down with increasing ATH concentration. It can be verified, however, that the presence of PP-VTES in the composite cuts down the decrease in the properties. These results are very important, since they show the effectiveness of the macromolecular coupling agent in improving the characteristics of the composites. It was not possible to observe any significant effect of varying the degree of functionalization and the concentration of PP-VTES on the mechanical properties of composites.

Thermogravimetric analysis was performed to investigate the behavior of the materials and particularly to ascertain the role of ATH and PP-VTES on the degradation of PP. Figure 11 shows the thermogravi-

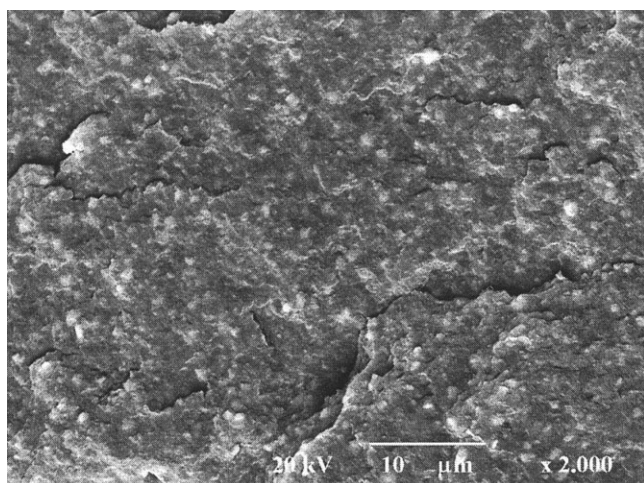


Figure 8 SEM micrograph of the composite PP/ATH/PP-VTESB (46.6/50/3.4).

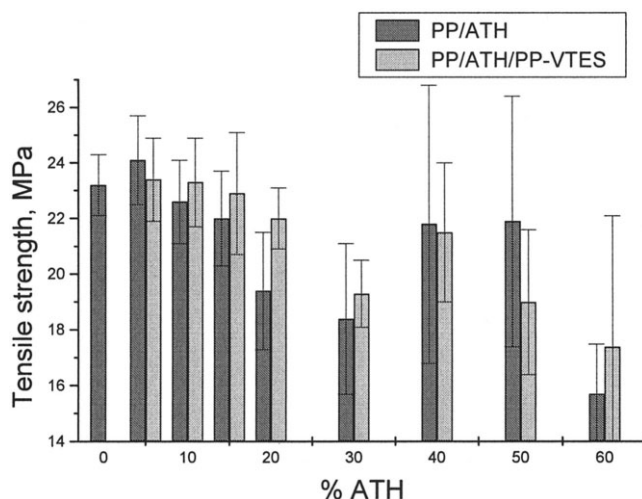


Figure 9 Tensile strength of the composites.

metric curves for PP and PP-VTES B, under nitrogen atmosphere. It was observed that both materials decomposed at a temperature ranging from 300 to 500°C in a single loss mass step, with the maximum decomposition peak around 470°C.

Shieh and Hsao²⁰ observed that the decomposition temperature of silane-grafted LDPE was much higher than that of LDPE. In that case, the authors attributed this result to the effect of crosslinking reactions of the silane grafts in the presence of a catalyst. In the present case, for the silane-grafted PP, it is supposed that no crosslinking had occurred since both temperatures were similar. It must be noticed that no extra degradation peak was observed, because of the alcoxysilane groups attached to the polymer chains in PP-VTES B.

When the neat PP, the PP/ATH, and the PP/ATH/PP-VTES composites were analyzed under nitrogen atmosphere, it was verified that the decomposition of

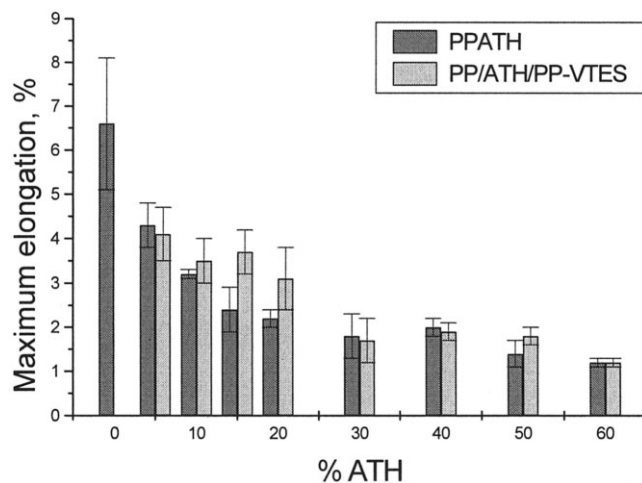


Figure 10 Maximum elongation of the composites.

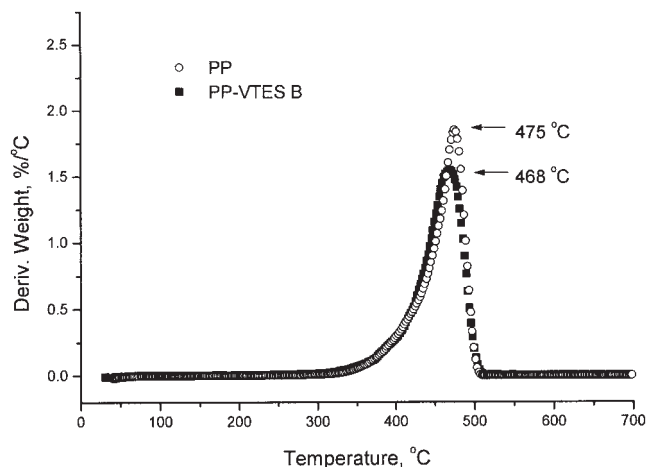


Figure 11 DTG versus temperature curves of PP and PP-VTES B under nitrogen.

PP occurred in the same temperature range. This means that the presence of ATH and PP-VTES did not affect the mechanism of PP decomposition in inert atmosphere (Fig. 12). However, a new small decomposition peak was observed near 300°C in the composites, corresponding to approximately 20% in weight of ATH employed. This decomposition peak can be attributed to water releasing from ATH in the presence of decomposing polymer.²¹ During combustion, the released water can absorb heat from the combustion zone, reducing the prospect of continued burning.

PP decomposition behavior was quite different when experiments were performed under oxidative atmosphere. Neat PP decreased its decomposition temperature under these experimental conditions, showing a maximum at about 320°C. On the other hand, the PP decomposition for all these PP composites was in the interval of 350–410°C. Even so, they were always lower than in nitrogen atmosphere (Fig. 13). These experimental results support the proposed mechanism for the flame retardant action of ATH. As water is released, a protective layer of aluminum oxide is formed, avoiding contact among the polymer and oxygen in such a way that its decomposition is retarded. Eventually, the released water can disrupt the protective layer, allowing the thermal decomposition to occur at a lower temperature than that observed under inert atmosphere.²¹ Because of the variability of results, no conclusions could be obtained about the role of PP-VTES in the decomposition under oxidative atmosphere.

PP composites, containing 40–60 wt % of ATH, were submitted to analysis of minimum oxygen concentration to sustain burning (LOI) and to flammability tests according to UL94 procedures. The experimental results (Table II) show that the minimum oxygen concentration to sustain burning increased with

ATH concentration. However, only composites containing 60% ATH plus the interfacial agent met the classification V0 according to UL94 procedures. Even though other composites did not sustain flame after removal of the burner, they could not get V0 classification since drops of the material were able to ignite a piece of cotton placed under the sample. So, they were classified as V2 grade, according to the technical procedure. PP composites containing 50 and 60 wt % ATH without the macromolecular coupling agent showed a lower classification than corresponding composites containing PP-VTES. This indicates that, apart from improving mechanical properties, the interfacial agent performed a positive effect on the flammability behavior.

CONCLUSIONS

PP composites, with upto 60 wt % ATH, were prepared in a mixer with the objective of obtaining composites with high flame retardancy and adequate mechanical properties. SEM micrographs showed well-dispersed systems with disruption of original ATH agglomerates. The presence of ATH reduced the PP melt flow index, tensile strength, and maximum elongation, but showed the deleterious effect of the mineral filler on the processability and mechanical properties of the polymer. Properties losses were greater for higher concentration of ATH.

VTES-modified PP, added to PP/ATH composites, had no appreciable effect on the processability of the materials; however, the tensile strength and maximum elongation were slightly improved, indicating that the modified polymer performs some beneficial interaction with the filler.

The decomposition temperature of PP in the composites did not change for tests performed under nitrogen when compared with the neat homopolymer.

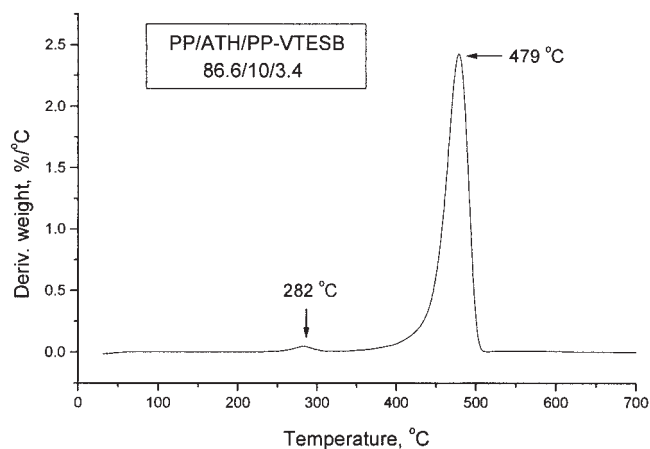


Figure 12 DTG versus temperature curve of a PP/ATH/PP-VTES B composite under nitrogen.

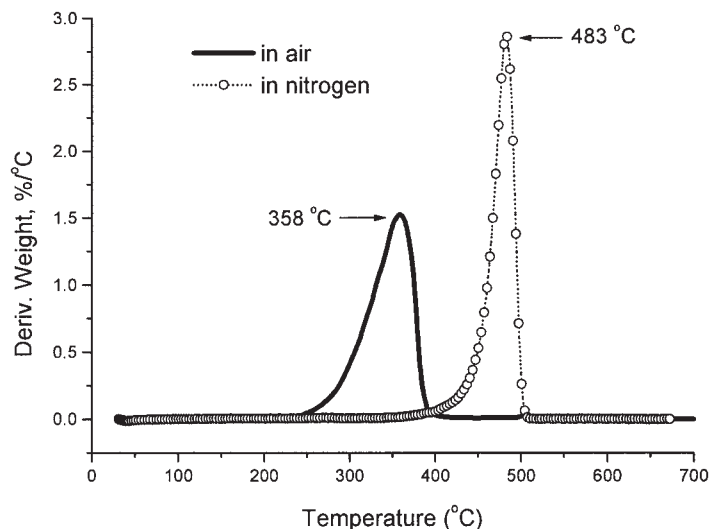


Figure 13 DTG curves of PP/ATH/PPVTES B (91.6/5/3.4).

However, it increased when tests were performed under air, probably because of the formation of a protective layer of oxide after the decomposition of ATH. The addition of PP-VTES did not interfere in the decomposition behavior of the composites in any case.

Composites containing PP-VTES showed the best results in flammability tests. Only that prepared with 60 wt % ATH plus PP-VTES achieved V0 classification according to UL94 procedures, with a 25% of limiting oxygen index.

The tensile properties and the flammability tests showed that PP-VTES can be employed as an effective coupling agent for PP/ATH composites.

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TABLE II

Limiting Oxygen Index (LOI) and UL94 Testing Results

PP (%)	ATH (%)	VTES (%)	LOI (%)	UL94
100.0	0	0	18	Fail
70.0	30.0	0	22	Fail
60.0	40.0	0	22	Fail
56.6	40.0	3.4	21	Fail
50.0	50.0	0	22	Fail
46.6	50.0	3.4	24	V2
40.0	60.0	0	25	V2
36.6	60.0	3.4	25	V0