

COMBINADA DE ADITIVOS DE ORIGEN BIOLÓGICO Y AGENTE DE ACOPLAMIENTO SOBRE LAS CARACTERÍSTICAS DE RETARDANCIA A LA FLAMA DE COMPUESTOS SOSTENIBLES DE POLIPROPILENO".

Sanchez-Valdes S, Martinez-Colungaa J.G., da Silva L., Lara-Sanchez J.

Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna No. 140, Saltillo, Mexico.
saul.sanchez@ciqua.edu.mx

Resumen: (e employed in polypropylene (PP) composites to enhance the flame-retardant (FR) properties. The combined effect of each additive and the use of functionalized PP with ammonium polyphosphate (PP-gAPP) as a compatibilizer, compared with PP-gMA, on composite FR properties was analyzed. This compatibilizer was prepared by melt reaction of maleic anhydride grafted PP (PP-gMA) with ammonium polyphosphate (APP). The grafting of APP was characterized by FTIR, XRD, and NMR. PP/KF/Ch composites using PP-gAPP as compatibilizer were characterized by TGA, mechanical properties, and fire-retardant tests such as UL-94 (HB), limiting oxygen index (LOI), and cone calorimeter evaluations. These tests demonstrated the enhancement in fire-retardant characteristics obtained by using PP-gAPP as a compatibilizer agent compared with PP-gMA. The combination of the additives (KF and Ch) with PP-gAPP as compatibilizer in PP, increases the modulus and tensile strength and significantly improves the LOI and reduces the peak heat release rate during cone calorimetry tests with better thermal stability and a noticeable reduction in horizontal burning rate. Most important, the results indicated that the combination of these additives produce similar flame retardancy than a reference sample with high magnesium hydroxide loading. These composites are a promising way to meet the growing demand for high-performance materials with FR characteristics using bio-fire retardant additives such as KF and Ch, in sustainable and environmentally friendly composites.

Introducción

Polypropylene (PP) is one of the highest consumption material worldwide. Its mechanical properties, even at elevated temperatures, are similar to those of an engineering polymer. PP is widely used in injection molded products for the automotive, electrical electronics, aerospace industries, building materials, and transportation, among others.^{1, 2} However, PP is considered a flammable material which strongly limits its uses.³ Therefore, developing a new environmentally friendly and effective flame-retardant (FR) agent is one of the most important methods to improve the flame retardancy of PP and its safety during its lifetime. Halogen-based additives have favorable FR properties, but they release highly corrosive halogenated compounds, Experimental

1 Materials used

PP homopolymer from Indelpro Inc. (Valtec-HP423M) with a melt index of 3.8 g/10 min

measured at 210°C and 2.16 kg. The maleic anhydride-modified polypropylene (PP-gMA) used as compatibilizer was from Uniroyal Chemicals (Polybond 3200), with 1.0 wt% MA; and 115 g/10 min. Chitosan powder with more than 90% of deacetylation was supplied by Marine Hydrocolloids. KF obtained from goose feathers with a bulk density of 0.8 g/cm³ and approximately 3 to 10 mm in length were milled and sieved to reduce their average size. APP treated with melamine-formaldehyde (APP104MF) with approximately 18 µm in particle size was purchased from Hangzhou JLS Flame Retardants Chemical. Finally, micrometric magnesium hydroxide (MH) from Albemarle, with an average particle size of 1.0 µm, was also used.

2.2 Fillers preparation

KF were obtained from cutting and milling poultry feathers. The feathers were washed with hot distilled water and dried at 80°C for 4 h. Subsequently, they were cut in a Brabender

blade mill at 3500 rpm.⁷ The KF and chitosan particles were grinded in a planetary mill for 10 min. Then, they were sieved for 10 min using a mesh with a pore diameter of 300, 212, 106, and 75 μm . The obtained final size of each filler is shown in Figure 1.

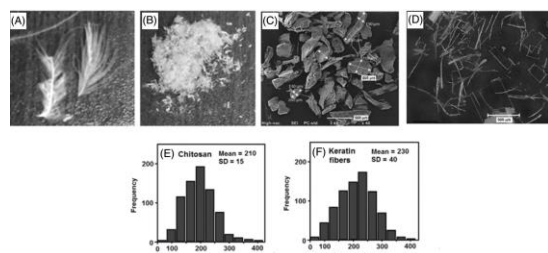


FIGURE 1 Images of: (A) pristine feathers, (B) milled feathers, (C) sieved keratin fibers (KF), (D) sieved chitosan particles and particle size Distribution for, (E) chitosan, and (F) KF Full Access

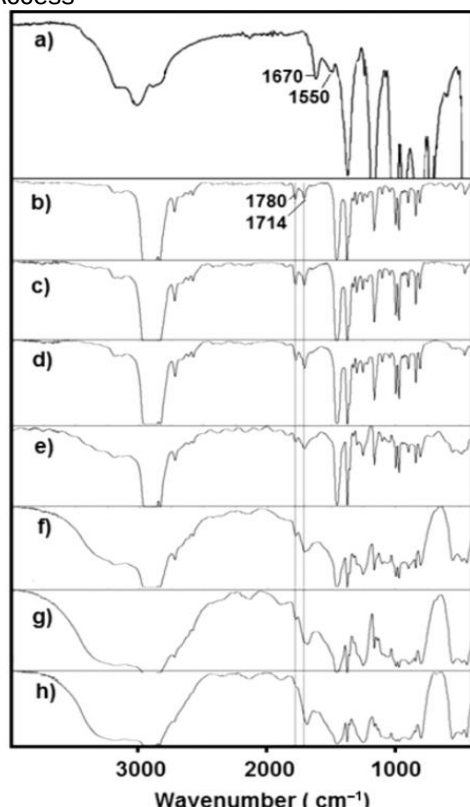


Figura 2. Espectros de FTIR (transmitancia) correspondientes a PPgMA y PPgAPP a diferentes relaciones en peso.

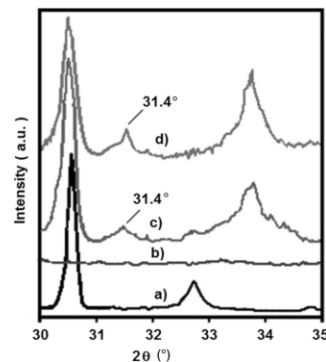


FIGURE 3 XRD of: (A) APP, (B) PP-gMA, (C) PP-gAPP 85/15 and (D) PP-gAPP 50/50.

2.4 Composites preparation

The composites were prepared by melt mixing incorporating the polypropylene, the compatibilizer, and the fillers using an Xplore extruder for 10 min, at 100 rpm and 190°C . The compatibilizer and the KF were used at 10 wt% concentration, whereas Ch was used at 20 wt%.^{8, 30} The PP-MH reference samples were prepared at 30 and 50 wt% of MH, which is commonly used in the wire and cable industry.⁵ Table 1 shows the prepared formulations.

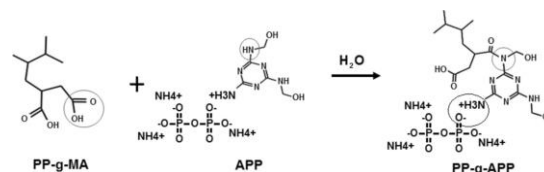


FIGURE 4 Scheme of the proposed structure of PP-g-APP.

RESULTS AND DISCUSSION

Figure 1 shows the grinded KF and the grinded chitosan particles used to prepare the composites. Also, this figure shows the average particle size of both types of fillers, chitosan with 210 μm and keratin with 230 μm . Based on the analysis of the fiber images, the aspect ratio of these was calculated as 1.6. These results are similar to those reported by Krystyna Wrzesniewska-Tosk et al.⁸ The PP-gAPP compatibilizer was obtained by melt mixing of PPgMA with APP in a 50/50 wt% ratio. To prepare the composites, 10 wt% of

this compatibilizer was used, which would represent 5 wt% of APP in the total mass. After mixing, the free unreacted APP will also contribute to flame retardancy. In the literature, it is reported that higher APP contents in polypropylene (10 to 30 wt%) would achieve good FR properties; however, these higher contents also would reduce the mechanical properties of the composite, by acting as a failure stress concentration. **Figure 2** shows the FTIR spectra of PP, PP-gMA, APP, and PP-gAPP samples. In Figure 2A,B comparing PP and PP-gMA, both samples show common signals between 2850 and 2970 cm^{-1} . TABLE 1 Formulation composition of prepared composite samples

TABLE 1 Formulation composition of prepared composite samples

sample	PP (wt%)	PP-gMA (wt%)	PP-gAPP (wt%)	Chitosan (wt%)	Kfiber (wt%)
PP	100	—	—	—	—
PP/Ch	80	—	—	20	—
/PP-gMA/Ch	70	10	—	20	—
PP/PP-gMA/KF	80	10	—	—	10
PP/PP-gMA/Ch/KF	60	10	—	20	10
PP/PP-gAPP/Ch	70	—	10	20	—
/PP-gAPP/KF	80	—	10	—	10
PP/PP-gAPP/Ch/KF	60	—	10	20	10

FIGURE 2 FTIR spectra of: (A) APP, (B) PP-gMA, PP-gAPP weight kW/m², using at least three specimens of each sample to determine: time of ignition, peak heat release rate, and total heat evolved. Water solubility of the samples was estimated as follows. A weighed sample (100 mg) was suspended in 100 ml distilled water and maintained under magnetic stirring at room temperature for 24 h. Then, the resulting solution was filtered in a positive pressure filter, and the precipitates were dried and weighed. The solubility of the sample in water was determined by the percentage of dissolved sample, which are

attributed to the symmetric and asymmetric stretching of the CH₃ and of the methyl and methylene, as well as, bending vibrations of CH₃ at 1380 cm^{-1} and CH₂ at 1460 cm^{-1} . On the other hand, in the PP-gMA spectrum, two characteristic bands at 1780 and 1714 cm^{-1} of C=O groups of the anhydride grafted onto the PP chain are observed. The melt mixing of PP-gMA and APP to obtain PP-gAPP was carried out at different APP concentrations: 0.2, 2.0, 15, 25, 33, and 50 wt%. Figure 2D–G show the FTIR spectra of selected samples of PP-gAPP composites compared to PP-gMA. It was observed that in samples with 0.2 wt% of APP (Figure 2D,E) show no significant changes in the FTIR bands. In contrast, in samples with 2.0 wt% of APP (Figure 2F) the carbonyl signal at 1714 cm^{-1} was intensified, probably due to the amidation reactions that occurred with the amines of the APP. In samples with 15 wt% of APP (85/15 wt%), Figure 2E, the broadening of the carbonyl signal is observed and a broad band at 3600–3100 cm^{-1} has appeared, attributed to the OH bending vibration that suggests a possible condensation. The sample with 25 wt% of APP (75/25 wt%), Figure 2F, shows an increase in the band corresponding to condensation and a new vibration band appears at 1690 cm^{-1} , probably attributed to the carbonyl of the amide. In the sample with 33 wt% of APP (67/33 wt%), Figure 2G, shows a growth of the absorption band corresponding to water and also that of the C=O of the amide is observed. In the sample with 50 wt% of APP (Figure 2H at 50/50 wt%), the C=O signal at 1714 cm^{-1} associated with the PP-gMA disappears and only the 1690 cm^{-1} signal of the carbonyl in the amide is observed.^{31,34} To emphasize the results obtained by FTIR, the samples were analyzed by XRD. The diffraction patterns of PP-gMA, APP, and the different formulations were compared and are shown in **Figure 3**. Figure 3A,B show the characteristic diffraction patterns of the APP and PP-gMA, respectively. It can be observed that at higher APP contents, a new diffraction signal appears at 31.4°, which intensifies as the APP content goes from 25 to 50 wt%. The diffraction patterns of PP-gMA/APP at 25 and 50 wt% of APP are shown in Figure 3C,D, where a new signal can be observed. The

appearance of this new diffraction signal suggests the presence of a new crystal configuration that does not belong to PP-g-MA or APP. These results support those.

Obtained by FTIR confirming the interactions between PP-gMA and APP and the formation of a new amine bond. According to the results obtained by FTIR, **Figure 4** presents the proposed structure of PP-gAPP that would result from the interaction between PP-g-MA and APP by a tertiary amination reaction. In addition to the inherent FR characteristics, the new coupling agent PP-gAPP has a greater number of polar and reactive sites for interaction with the additives that are to be added, such as keratin and chitosan. The PP-gAPP with 50 wt% of APP was chosen because it showed higher interaction between PP-gMA and APP, which would allow a good balance between the improvement of the flame retardancy properties and the compatibility effect between the incorporated additives and the polymeric matrix.

To verify the proposed chemical structure of the obtained PPgAPP, NMR was performed in a solution of Xylene and PP-gAPP at 40 mg/ml using a deuterated toluene capillary for the measurement of ^1H and ^{13}C . **Figure 5** shows the NMR spectrum of ^1H and ^{13}C for the obtained PP-gAPP. The signal at 11 ppm in ^1H corroborates the structure of the carboxylic acid COOH and in ^{13}C , the signal at 165 ppm corresponds to the amide.³⁵ While the rest of the structure signals cannot be determined as they overlap with deuterated toluene and Xylene, the appearance of two of the fundamental parts of the PP-gAPP structure, the carboxylic acid and the amide, confirms that PP-gAPP was obtained.

Composites characterization

Previous analysis to determine the possible degradation of PP during the preparation of the composites was carried out by measuring the change in PP molecular weight before and after the extrusion process at working conditions. Table 2 shows that no significant change in the PP molecular weight was observed suggesting that minor PP degradation occurred at the extrusion conditions used to prepare the composites.

TGA results

Table 2 Peso molecular promedio en peso de PP y PP extruido

	Mw (g/mol)
PP	374188
PP procesado	358152

The obtained PP-gAPP was characterized by TGA to analyze its thermal stability. **Figure 5A** shows the thermal behavior of PP and the two modified PPs, where it can be observed that PP-gAPP showed a significant thermal stability compared with PP-gMA. It can be seen that PP and PP-gMA show a very similar decomposition behavior. PP sample begins its decomposition at 300°C and PP-gMA at 305°C, where as PP-gAPP begins its decomposition at 410°C, confirming the better thermal stability provided by the APP. The thermal stability for the various composites can be seen in Figure 5B. Composite samples with no compatibilizer and reference samples with 30 and 50 wt% MH can be observed in this figure. The thermal behavior of PP/Ch composite without compatibilizer, occurred in two stages; the first one takes place below 110°C, and is attributed to the evaporation of the residual water. The second degradation step occurs between 200 and 340°C, which is attributed to the decomposition of the polymer chains. The overall weight loss after the second step is mainly associated with the decomposition and polymerization of chitosan. Meanwhile, the PP/KF sample without compatibilizer first produces volatile gases, loosely bonded and strong-bonded water at temperatures below 300°C, followed thereafter by keratin degradation of disulfide bridges and other S-containing compounds in the proteins. Comparing these PP composites with the reference samples with 30 and 50 wt% of MH, it can be seen that increase the smoke and CO production during combustion. Some specific halogen additives have been forbidden in several countries for specific applications.

Halogen-free flame retardancy has been obtained by the incorporation of metal hydroxides, typically aluminum trihydrate $[\text{Al}(\text{OH})_3]$ or magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ into the polymer matrix.

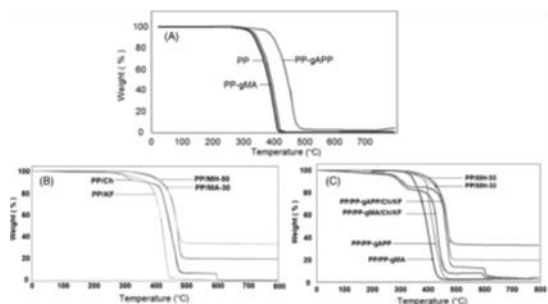


FIGURE 5 TGA thermograms for: (A) PP and compatibilizers, (B) uncompatibilized composites, and (C) compatibilized composites.

These metal hydroxides, commonly require high loading levels leading to a negative effect on polymer performance. The use of flame retardants of biological origin is an interesting alternative that reduces the flammability of polymers and contributes with nontoxic and sustainable materials to reduce the environmental contamination problem. In this context, chitosan and keratin fibers (KF) have been shown to have FR properties. An additional advantage of these materials is that they are environmentally friendly with lower costs than conventional intumescent agents because they are commonly obtained from waste or by-products of the food industry. Chitosan is the second most abundant natural biomaterial after cellulose. It is extracted from the shell of crustaceans and in solid form it is a crystalline, nontoxic, biodegradable, and biocompatible polymer. It is obtained from the extraction of chitin through a deacetylation process, forming an amino-polysaccharide with hydroxyl groups in its structure. Chitosan is a material with excellent FR properties which are mostly attributed to the formation of a protective char layer, related to its inherent polysaccharide structure. This FR properties need to be reinforced with other additives to ensure its FR for long periods of flame exposure. This char layer acts as a barrier to the oxygen diffusion into the material and to the emission of toxic gases generated during combustion. Chitosan has also been used as a reinforcement in many polymer composites, although certain difficulties have been encountered due to the lack of compatibility between the polymer and chitosan phases. On the other hand, KF has also demonstrated FR

properties and has been used in applications as reinforcement of polymeric matrices. It can be obtained from the hair, bird feathers, horns, hooves, etc., which are a by-product of the food industry. Keratin has very interesting properties such as low cost and its proven effect as FR in polyurethanes and elastomers. In addition, it has a low-density fibrillar structure that has been proven to be an efficient polymer reinforcement with additional characteristics of biodegradability. Being a protein, it has a complex amino acid structure that contributes to the formation of phenol and aromatic compounds with greater thermal stability. KF is also rich in nitrogen, which is necessary for an efficient intumescent effect. The FR mechanism of keratin is based on the formation of an intumescent carbonaceous char layer, liberating nitrogen gas that foams during combustion. This foam layer isolates the material, delaying the oxygen diffusion and the release of toxic gases formed during combustion. Various techniques have been used to avoid filler or additive particles agglomeration in polymeric matrices, such as the use of coupling or compatibilizing agents. The use of maleic anhydride functionalized polyolefin has been widely reported as an efficient coupling agent that improves the particle dispersion and the final composite performance. A remarkable improvement in the FR of polyethylene reinforced with KF and deoxyribonucleic acid has been reported when using maleic anhydride functionalized polyolefins as a coupling agent. During combustion, an intumescent material is produced, forming a significant volume of insulating carbonaceous foam that protect the polymer matrix and inhibits the propagation of heat, oxygen, and mass loss. To obtain an intumescent FR system, the combination of an acid source, a charring agent and a foaming agent are required. The acid source helps to carbonize the carbonaceous source and together with the gases released by the foaming source a foamed char protective layer is produced. Ammonium polyphosphate (APP) can act as a flame retardant in the condensed or polymer phase through intumescence. During this intumescence action, a material swells when it is exposed to heat during burning to form a porous carbonaceous foam

which acts as an isolating barrier to prevent heat, air and pyrolysis products from entering the surface of the material. In this work, APP grafted polypropylene (PP-gAPP) was obtained by the melt reaction of maleated PP (PP-gMA) with APP. This PP-g APP was used as a coupling agent between KF and chitosan with a PP matrix to analyze the effect on the flame retardancy and mechanical properties. Also, the possible interactions between the polar groups of the coupling agent and the groups present in the chitosan and keratin fillers, are described, through amidation and esterification reactions among other interactions. This approach provides a promising way to replace the conventional halogen fire-retardant hazardous compounds, with bio-fire-retardant additives in environmentally sustainable composites with good mechanical and fire-retardant properties. The so-obtained composites could have a good potential for the design of effective FR systems.

The UL-94HB test involves placing the specimen at a horizontal angle of approximately 45° and measuring the burning rate once ignited. When burning, the specimen consumes the flame homogeneously and perpendicularly along its length. In contrast, if a specimen exhibits flame-resistant properties, meaning it resists being consumed, its burning rate is slow, it does not consume homogeneously, and it forces the fire to spread to the upper part of the specimen until it is extinguished. The PP/PPgAPP/Q/FK system performed best, with the lowest burning rate (7.04 mm/min), exceeding the industry standard. This performance was due to the additives (chitosan and keratin fiber) which, together with the PPgAPP, promoted the formation of a carbonaceous layer that protected the material (Figure 12).

Table 4 shows that compounds containing PPgAPP with chitosan or keratin fiber, and the combination of both, exhibited lower burn rates, exceeding the reference values. In contrast, systems with PPgMA with the additives (Q or FK), and the combination of both, burned faster than those containing PPgAPP and yielded burn rates close to the reference values.

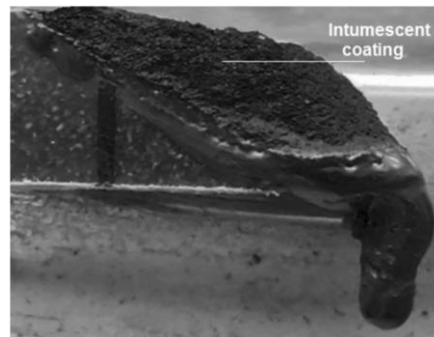


FIGURE 6 Image of the char coating formed after the burning rate determination for PP/PP-gAPP/Ch/KF composite sample (588.5/1580.1-1x=62.7%.

Sample	pHRR (kW/m ²)	Change ^a (%)	TTI (s)	THR (MJ/m ²)
PP (100)	1580.1 ± 11	0	38	109.9 ± 09
PP/MH (50/50) Reference	588.5 ± 03	-62.7	43	88.9 ± 05
PP/PP-gMA (90/10)	1857.9 ± 09	17.5	36	113.9 ± 03
PP/PP-gAPP (90/10)	1182.9 ± 07	-25.1	46	92.7 ± 08
PP/Ch (80/20)	1336.8 ± 05	-15.5	35	99.7 ± 06
PP/KF (80/20)	1490.6 ± 08	-6.7	34	103.3 ± 10
PP/PP-gMA/Ch (70/10/20)	1342.5 ± 06	-15.0	34	99.2 ± 03
PP/PP-gMA/KF (80/10/10)	1780.7 ± 10	12.6	33	105.5 ± 08
PP/PP-gMA/Ch/KF (70/10/20/10)	1274.3 ± 07	-19.3	34	93.2 ± 05
PP/PP-gAPP/Ch (70/10/20)	845.7 ± 03	-46.4	39	91.8 ± 03
PP/PP-gAPP/KF (80/10/10)	1379.2 ± 06	-13.2	37	105.1 ± 03
PP/PP-gAPP/Ch/KF (70/10/20/10)	605.3 ± 04	-61.6	44	89.7 ± 02

Conclusiones.

Composites of PP with combinations of KF and Ch compatibilized with PP-gAPP were obtained with excellent FR properties. PP-gAPP obtained from the reaction of PP-gMA with APP enhanced the FR properties of PP composites. The incorporation of PP-gAPP to PP composites with KF or Ch reduces the burning rate of PP, due to the intumescence and FR characteristics of APP. Composites with PP-gAPP reduced the BR and increased the LOI and rendered better cone calorimeter results that confirm the excellent FR properties induced by APP. A noticeable effect in the FR properties of each of the composite components was observed. PP-gAPP showed a better compatibilizing effect increasing the mechanical properties and the flame retardancy than PP-gMA. The composite of PP with Ch and KF compatibilized with PP-gAPP showed similar FR performance than a

reference PP-MH sample with 50 wt% MH loadings. This composite formed a similar char coating protective layer to the reference sample.

REFERENCES

1. Zhang F, Wang Y, Jin Y, Zhang J. Simulated effects of physical parameters on heat transfer of intumescent fire-retardant polypropyleneduring burning. *J Macromol Sci Part Phys B*. 2011;50:1185-1195.
2. Shao ZB, Deng C, Tan Y, Chen MJ, Chen L, Wang YZ. Flame retardation of polypropylene via a novel intumescent flame retardant: ethylenediamine-modified ammonium polyphosphate. *Polym Degrad Stab*. 2014;106:88-96.
3. Zhang S, Horrocks AR. A review of flame retardant polypropylenefibres. *Progr Polym Sci*. 2003;28(11):1517-1538.
4. Mai Nguyen TT, Prabhakar MN, Song JI. Influence of biowaste additive and treated short woven flax fibers on the flame retardancy and mechanical properties of PP composites. *Ind Crops Prod*. 2021;174:114176.
5. Hollingbery LA, Hull TR. The fire retardant behaviour of huntite and hydro magnesite – a review. *Polym Degrad Stab*. 2010;95:2213-2225.
6. Tittleman GI, Gonen Y, Keidar Y, Bron S. Discoloration of polypropylene based compounds containing magnesium hydroxide. *Polym Degrad Stab*. 2002;77:345-352.
7. Zhong H, Wu D, Wei P, Jiang P, Li Q, Hao J. Synthesis, characteristic of a novel additive-type flame retardant containing silicon and its application in PC/ABS alloy. *J Mater Sci*. 2007;42:10106-10112.
8. Wrzesniewska-Tosk K, Zajchowski S, Bryskiewicz A, Ryszkowska J. Feathers as a flame-retardant in elastic polyurethane foam. *Fibers Text East Eur*. 2014;22:119-128.
9. Wang L, Yoshida J, Ogata N, Sasaki S, Kajiyama T. Self-assembled supramolecular films derived from marine deoxyribonucleic acid (DNA) cationic surfactant complexes: large-scale preparation and optical and thermal properties. *Chem Mater*. 2001;13(4):1273-1281.
10. Yang Z, Li H, Niu G, Wang J, Zhu D. Poly(vinyl alcohol)/chitosan-based high-strength, fire-retardant and smoke-suppressant composite aero-gels incorporating aluminum species via freeze drying. *Compos Part B: Eng*. 2021;219:108919.
11. Kong Q, Wu T, Zhang H, et al. Improving flame retardancy of IFR/PP composites through the synergistic effect of organic montmorillonite intercalation cobalt hydroxides

modified by acidified chitosan. *Appl Clay Sci*. 2017;146:230-237.

12. Kuru D, Akpınar-Borazan A, Guru M. Effect of chicken feather and boron compounds as filler on mechanical and flame retardancy properties of polymer composite materials. *Waste Manage Res*. 2018;36(11):1029-1036.
13. Shi X, Jiang S, Hu Y, Peng X, Yang H, Qian X. Phosphorylated chitosan-cobalt complex: a novel green flame retardant for polylactic acid. *Polym Adv Technol*. 2018;29:860-866.
14. Donato RK, Mija A. Keratin associations with synthetic, biosynthetic and natural polymers: an extensive review. *Polymers*. 2020;12(1):32. doi:10.3390/polym12010032
15. Davies PJ, Horrocks AR, Mirafteb M. Scanning electron microscopic studies of wool/intumescent char formation. *Polym Int*. 2000;49:1125-1132.
16. Raji M, El Mehdi Mekhroum M, Rodrigue D, El Kacem Qaiss A, Bouhfid R. Effect of silane functionalization on properties of polypropylene/clay nanocomposites. *Compos Part B: Eng*. 2018;146:106-115.
17. Albite-Ortega J, Sánchez-Valdes S, Ramírez-Vargas E, et al. Influence of keratin and DNA coating on fire retardant magnesium hydroxide dispersion and flammability characteristics of PE/EVA blends. *Polym Degrad Stab*. 2019;165:1-11.
18. Li X, Yang J, Zhou X, et al. Effect of compatibilizer on morphology, rheology and properties of SEBS/clay nanocomposites. *Polym Test*. 2018;67:435-440.
19. Dasari A, Yu ZZ, Cai GP, Mai YW. Recent developments in the fire retardancy of polymeric materials. *Prog Polym Sci*. 2013;38:1357-1387.
20. Stefani D, Dahlem MA, Francisquetti EL, et al. Influence of coupling agent on post-consumption polypropylene composites reinforced with malt bagasse fibers. *J Compos Mater*. 2021;55:4333-4346.
21. Zabihi O, Ahmadi M, Li Q, et al. A sustainable approach to scalable production of a graphene based flame retardant using waste fish deoxyribonucleic acid. *J Clean Prod*. 2020;247:119150.
22. Alongi J, Carletto RA, Di Blasio A, Carosio F, Bosco F, Malucelli G. DNA: a novel, green, natural flame retardant and suppressant for cotton. *J Mater Chem*. 2013;1:4779-4785.
23. Alongi J, Cuttica F. DNA coatings from byproducts: a panacea for the flame retardancy of EVA, PP, ABS, PET, and PA6? *ACS Sustain Chem Eng*. 2016;4:3544-3551.
24. Alongi J, Di Blasio A. Flame retardant properties of ethylene vinyl acetate copolymers melt-compounded with deoxyribonucleic acid in the presence of α -cellulose or β -cyclodextrins. *Curr Org Chem*. 2014;18:1651-1660.

25. Bourbigot S, Le Bras M, Duquesne S, Rochery M. Recent advances for intumescent polymers. *Macromol Mater Eng.* 2004;289:499-511.
26. Le Bras M, Bourbigot S, Revel B. Comprehensive study of the degradation of an intumescent EVA-based material during combustion. *J Mater Sci.* 1999;34(23):5777-5782.
27. Jung D, Bhattacharyya D. Combined effect of silicate coating and phosphate loading on the performance improvement of a keratinous fiber-based flame retardant. *Chem Eng J.* 2021;424:130484.
28. Beyer G. Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminium trihydrate. *Fire Mater.* 2001;25:193-197.
29. Laachachi A, Ferriol M, Cochez M, Cuesta JML, Ruch D. A comparison of the role of boehmite (AlOOH) and alumina (Al₂O₃) in the thermal stability and flammability of poly(methyl methacrylate). *Polym Degrad Stab.* 2009;94:1373-1378.
30. Mir S, Yasin T, Halley PJ, Siddiqi HM, Nicholson T. Thermal, rheological, mechanical and morphological behavior of HDPE/chitosan blend. *Carbohydr Polym.* 2011;83:414-421.
31. Wu Q, Qu BJ. Synergistic effects of silicotungstic acid on intumescent flame retardant polypropylene. *Polym Degrad Stab.* 2001;74(2):255-261.
32. Lin H, Yan H, Liu B, Wei L, Xu B. The influence of KH-550 on properties of ammonium polyphosphate and polypropylene flame retardant composites. *Polym Degrad Stab.* 2011;96(7):1382-1388.
33. Jiang W, Hao J, Han Z. Study on the thermal degradation of mixtures of ammonium polyphosphate and a novel caged bicyclic phosphate and their flame retardant effect in polypropylene. *Polym Degrad Stab.* 2012;97(4):632-637.
34. Caicedo C, Arce AV, Crespo LM, de la Cruz H, Ossa OH. Material compuesto de matriz polipropileno (PP) y fibra de cedro: influencia del compatibilizante PP-g-MA. *Informador Técnico.* 2015;79(2):118-126.
35. Ma J, Shang Y, Peng C, et al. Synthesis, characterization, and performance of novel phosphate-modified polymers as air-entraining agents. *Constr Build Mater.* 2020;232:117231.
36. Lim K, Bee S, Sin LT, et al. A review of application of ammonium polyphosphate as intumescent flame retardant in thermoplastic composites. *Compos Part B: Eng.* 2016;84:155-174.
37. Dahiya JB, Kumar N, Bockhorn H. Fire performance and thermal stability of polypropylene nanocomposites containing organic phosphinate and ammonium polyphosphate additives. *Fire Mater.* 2014;38:1-12.
38. Chen B, Fang Y, Si Y, et al. Flame retardancy of ammonium polyphosphate-chitosan/boron nitride on plywood surface via layer-by-layer self-assembly method. *Acta Mater Compos Sin.* 2021;38(4):1252-1261.
39. Lujan-Acosta R, Sánchez-Valdés S, Ramírez-Vargas E, et al. Effect of amino alcohol functionalized polyethylene as compatibilizer for 180 ALBITE-ORTEGA ET AL. LDPE/EVA/clay/flame-retardant nanocomposites. *Mater Chem Phys.* 2014;146:437-445.
40. Sánchez-Valdés S, Ramírez-Vargas E, Rodríguez-González JA, et al. Organopolysulfide and molybdenum sulfide combinations to produce mechanical and processing enhanced flame-retardant PE/EVA blend composites with low magnesium hydroxide loading. *J Vinyl Addit Technol.* 2020;26(4):434-442.
41. Wang Y, Shi Y, Shao W, et al. Crystallization, structures, and properties of different polyolefins with similar grafting degree of maleic anhydride. *Polymers.* 2020;12:675. doi:10.3390/polym12030675
42. Thwe M, Liao M. Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Compos Sci Technol.* 2003;63:375-387.
43. Wong B, Baker WE. Melt rheology of graft modified polypropylene. *Polymer.* 1997;38(11):2781-2789.
44. Sain M, Park SH, Suhara F, Law S. Flame retardant and mechanical properties of natural fibre-PP composites containing magnesium hydroxide. *Polym Degrad Stab.* 2004;83:363-367.