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Research Article

Mechanochemistry for the Synthesis of a Sustainable Phosphorus/Potassium Tannic Acid Flame-Retardant Additive and Its Application in Polypropylene

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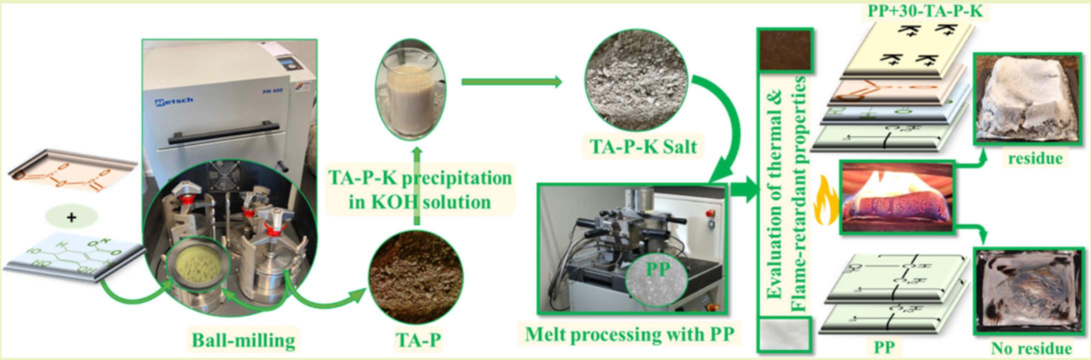

ABSTRACT: Tannic acid (TA) is an abundant biobased aromatic compound that can form char under thermal degradation and fire conditions. In the present study, TA was chemically modified by grafting potassium phosphate groups using a two-step process, requiring neither heating nor organic solvents. Initially, TA was functionalized through ball-milling mechanochemistry in the presence of P_2O_5 to graft phosphoric acid, which was later converted to potassium phosphate salt by simple precipitation in water in the presence of KOH. The reaction yield was 87%. The resulting product, namely, TA-P-K, was used as a flame retardant (FR) in polypropylene (PP). At 30 wt %, TA-P-K was dispersed in PP by melt processing, resulting in a significant reduction in the peak heat release rate of 78% measured by the mass loss cone calorimeter test. Additionally, an intumescent residue was formed during combustion, which protected the material. In terms of flame-retardancy performance, the polymer composite took a "*Good*" label based on *Flame-Retardancy Index* (*FRI*), which seems promising in view of FR being fully biobased.

KEYWORDS: *mechanochemistry, tannic acid, phosphorylation, flame retardancy, metallic salt*

INTRODUCTION

Combustible polymeric materials became ubiquitous in the second half of the twentieth century, and their use has been extended to various daily applications. To minimize fire risk and meet fire safety requirements, flame-retardant solutions have been developed to prevent the ignition of polymers, to lower the heat rate released during their combustion, and to limit flame propagation. These additives interfere in physical or chemical processes involved in polymer combustion.[1] As environmental concerns related to climate change and greenhouse gas emissions increase, there is increasing interest in finding new ways to reduce the carbon footprint of materials.[2] The development of biobased materials and additives by improving or creating new functionalities for plastics is known as an efficient way to reduce the environmental impact of polymeric materials while preserving their technical performances. Among them, sustainable biobased flame retardants (FR) produced from renewable resources can support the increasing use of low-carbon-focal-rate materials across many technical applications. Indeed, some biomass constituents such as cellulose, lignin, or tannins are even predisposed to be used as fire-retardant additives, due to their chemical composition and structure, providing them with the inherent ability to produce charred residues upon fire exposure.[3]

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The char-forming ability is particularly relevant for the development of effective condensed-phase FR systems. During the combustion process, the burning of the FR and producing char generate an insulating layer formed at the surface of the burning materials, which improves the fire-retardant behavior by reducing the thermal and oxygen diffusion as well as the amount of combustible volatile compounds. However, it comes out that biobased char-forming additives need to be either combined with other flame-retardant products or chemically modified prior to being able to produce thermally resistant char structures under thermooxidative degradation. Traditionally, FRs are prepared through liquid-phase organic synthesis, which usually requires the use of solvents and subsequent complex purification multisteps, negatively impacting their sustainability. Therefore, there is a strong need to develop more efficient and environmentally friendly approaches for the preparation of sustainable biobased FRs.

Biobased aromatic compounds such as lignocellulosic materials are highly promising for the development of FRs.[3] Lignin has demonstrated an appropriate flame-retardant effect in various polymers such as PP,[4] polylactide (PLA),[5−7] and polybutylene succinate (PBS),[8] whether combined with other FRs or chemically modified. However, the fire performance with lignin is variable because of its intrinsic polymeric structure, which varies according to its botanical origin and the type of extraction process used. The large molecular weight distribution and variability in terms of reactivity and composition are a few to name, which are the main obstacles to adoption of lignin as an efficient FR. The use of oligomeric or structurally stable aromatic derivatives overcomes the variability problems observed with lignin.

Tannins are another family of phenolic compounds that are present in the bark of trees and provide them with fire protection owing to their appropriate char-forming ability.[9] Tannins are classified into hydrolyzable and nonhydrolyzable or condensed tannins. Hydrolyzable tannins present well-defined structures in contrast to condensed tannins, which have oligomeric and polymeric complex structures.[10] TA is a type of polyphenol tannin with properties that are relevant to flame-retardant applications. It is an abundant commercially available biobased raw material, with a well-known and invariable chemical structure containing several reactive sites. Numerous studies have demonstrated the effectiveness of TA as FR, either in combination with other FRs such as ammonium polyphosphate[11] or through its chemical derivatization for grafting phosphorus-based compounds.[12,13]

In a previous work, we demonstrated that the chemical modification of TA with phosphorus chloride in chloroform for 16 h at 60 °C significantly increased its char-forming ability.[12] The incorporation of this phosphorylated TA into polylactide (PLA) proved to greatly enhance the flame-retardant properties of the resulting composites. Nevertheless, because of the modification process parameters, the sustainability of this biobased FR has been greatly reduced. The environmental impact of the chemical process used for derivatizing TA could be reduced in three pathways by eliminating organic solvents (chloroform), using other phosphorus reagents that do not form any byproducts during the chemical derivatization reaction, and reducing the reaction temperature and duration.

Mechanochemistry appears to be the most appropriate approach for limiting the negative impacts of the derivatization process. The field of mechanochemistry is dedicated to understanding and exploiting the impact of mechanical actions on chemical reactions.[14,15] By simple grinding of solid reagents with a mortar and pestle, several chemical reactions can be significantly accelerated. In organic chemistry and materials synthesis, mechanochemistry is becoming increasingly popular because of its ability to reduce solvent waste generation and energy consumption.[16,17] Ball-milling is an appropriate technique for mechanochemistry imposing shear forces generated by high-speed rotation and temperature increase,[18,19] in addition to its advantages like easy processing, low cost, and capacity to process high volumes. Originally, the use of ball-milling in the preparation of FRs was limited to grind powders in order to reduce their particle size and increase their surface area to obtain composites with good mechanical properties and easy melt processing. Since then, ball-milling has become increasingly widespread and used for the synthesis of novel FRs through chemical reactions, including solvent-free solid−solid reactions, as the heat and force generated by ball-milling were sufficient for some of these reactions.

Among various chemical modifications, phosphorylation represents a major reaction in the field of flame retardancy. Generally, grafting phosphorus onto additives or polymers promotes the formation of a protective char layer during thermal degradation. Fiss et al.[20] studied the phosphorylation of cellulose nanocrystals, lignin, and different synthetic polymers including poly(ethylene glycol), poly(vinyl alcohol), and poly(vinyl chloride) by ball-milling mechanochemistry using phosphorus pentoxide, with the aim of producing reproducible phosphorylation for potential flame-retardant applications and avoiding the use of organic solvents and elevating temperatures. The so-called phosphorylated materials exhibit notable flame-retardant properties. Piao et al.[21] prepared lignocellulosic-based P-N additives (LFPN) by ball-milling the lignocellulosic fibers and ammonium polyphosphate into deionized water (at room temperature for 10 h) via a mechanochemistry approach. The supernatant with 4% LFPN was recovered by centrifugation and applied as a coating on a cotton fabric. Based on the obtained results, it can be concluded that the treated fabric demonstrated superior FR properties in different fire tests owing to the condensed-phase action of the FR system.

In light of the above investigations, we amalgamated the idea of using mechanochemistry for developing FRs with the need for novel biobased FRs from sustainable resources and reagents. In this work, a novel biobased flame-retardant additive, namely, potassium phosphate TA salt (TA-P-K), was prepared via mechanochemistry. A two-step preparation process based on (i) ball-milling mechanochemistry of TA and P_2O_5 followed by (ii) metallic salt precipitation in water (with KOH) was applied. This novel biobased flame-retardant agent (TA-P-K) was characterized using thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), and inductively coupled plasma analysis (ICP). TA-P-K incorporated into polypropylene (PP) at 30 wt % by melt blending. The effect of its incorporation on the thermal and flame-retardant properties of PP was investigated using TGA, cone calorimetry, and smoke opacity tests.

■ EXPERIMENTAL SECTION

Materials. A high impact-modified polypropylene copolymer (PP 402 CB12) was provided by INEOS Olefins & Polymer Europe. This grade is adapted for injection-molding applications and is characterized by a melt flow rate (230 C, 2.16 kg) of 12 g/10 min,

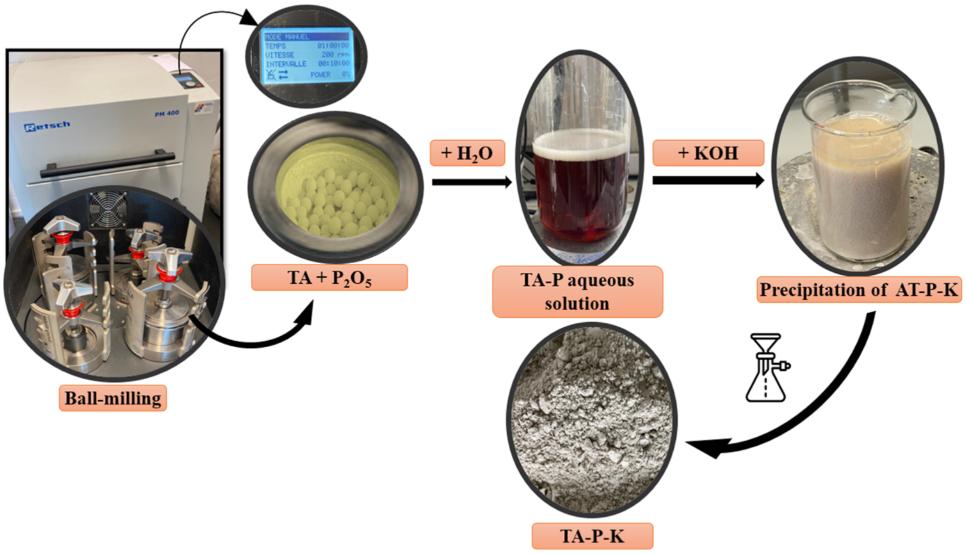

Figure 1. Schematic presentation of mechanochemistry applied in TA modification by ball-milling and KOH aqueous precipitation.

tensile strength at yield = 25 MPa, and Izod impact strength = 6 and 10 kJ·m^{-2} (at −20 and +23 C, respectively). PP 402 CB12 was abbreviated as "PP". TA, phosphorus pentoxide (P_2O_5, purity 99%), and potassium hydroxide were purchased from Sigma-Aldrich.

METHODS

Preparation of Modified Tannic Acid. TA was modified by P_2O_5 by ball-milling using Planetary Ball Mill PM 400 equipment from Retsch (Germany). 42 g of TA and 8.7 g of P_2O_5 were incorporated in a 500 mL stainless steel jar with 60 stainless steel balls (3 g/ball) at room temperature. The mill process was applied for 1 h with a 30 s rest every 10 min. After milling, the resulting mixture was collected and named TA-P. The recovered TA-P underwent a second modification by precipitation. A KOH aqueous solution (0.5 M) was added to TA-P media, under vigorous mechanical stirring, until pH 7 was reached. The decision to use KOH over other bases was a result of a selection process. Among the other bases tested (NaOH, NH_3OH), KOH formed a precipitate the fastest and in the largest quantities. The recovered salt was filtered, dried, and named TA-P-K (Figure 1). It is important to note that neither organic solvents nor heating were required in this modification process. The product was then dried and was ready for use. Additionally, this synthesis route takes advantage of transforming water-soluble TA and phosphorylated TA (TA-P) into an insoluble salt that prevents FR migration from the polymer during its lifetime.

The amount of P_2O_5 mixed with TA in ball-mill jars corresponded to a total phosphorus content of approximately 7.55 wt %. This corresponded to the P content of TA-P since this product had not undergone any purification step. ICP analysis of the final TA-P-K product indicated that it contained 2.0 wt % phosphorus and 7.6 wt % potassium (Table 1). The KOH precipitation step removed all of the phosphorus that had not reacted with TA. Moreover, it is worth mentioning that the phosphorus content obtained using ball-milling chemistry was even greater than that obtained in our previous study,[12] i.e., 1.75 wt % using a solvent-based chemical modification process and 16 h of reaction time.

Table 1. UL-94 Classification Requirements

classification	afterflame time (s)	total sum of afterflame times (s)	burning drips	burn to the clamp
V_0	<10	<50	no	no
V_1	<30	<250	no	no
V_2	<30	<250	yes	no

Composites Preparation. Blending of TA and derivatives within the molten PP was carried out using a Brabender bench-scale kneader (Brabender GmbH &. Co. KG, Duisburg, Germany) at 180 °C (3 min mixing at 30 rpm and 7 min at 90 rpm). PP and additives were previously dried in an oven at 60 °C overnight. Plates for cone calorimeter (100 × 100 × 3 mm^3) and smoke density (50 × 50 × 3 mm^3) tests were prepared using an Agila PE20 hydraulic compression molding press at 180 °C. The sample is first deposited for 3 min on the hot part and pressed for 1.5 min at 50 bar, followed by 3 degassing, pressed again for 3 min at 150 bar, and deposited in the cold part where it is pressed for 5 min.

Analyses and Characterizations. FTIR spectra were recorded using a Bruker α II spectrometer, in the wavelength range from 4000 to 400 cm^{-1}, with 2 cm^{-1} resolution and an accumulation of 32 scans.

Inductively coupled plasma (ICP) analysis was used for the determination of the amount of phosphorus and potassium in the modified TAs and was performed with an Optima 7300dV ICP-OES instrument from PerkinElmer. Prior to ICP analysis, the sample was digested by using nitric acid. The amounts of phosphorus and potassium were determined by using calibration curves obtained from ICP analyses of standard solutions at different concentrations (5 and 10 ppm) in combination with TA.

Thermal decomposition of TA, its chemically modified derivative, pristine PP, and all related composites was studied by thermogravimetric analysis (TGA) using TGA II equipment from Mettler Toledo. Approximately 5 mg of the sample was subjected to a temperature ramp from 100 to 700 °C at a heating rate of 10 °C·min^{-1} under nitrogen (80 mL·min^{-1}). The residual weights at 350 and 700 °C as well as the temperature corresponding to 5% mass loss (T_{-5}) were determined.

Scanning electron microscopy−energy-dispersive X-ray analysis (SEM−EDX) was used to evaluate the dispersion of TA-P-K, as well as P and K atoms, through the composite. Analysis was conducted on a Hitachi SU-8020 instrument (Hitachi, Tokyo, Japan).

A mass loss cone calorimeter (MLC) from Fire Testing Technology was used according to ISO 5660 standard procedures to evaluate the fire behavior of different compositions. Samples (100 × 100 × 3 mm^3) were exposed to an external heat flux of 35 kW·m^{-2}, corresponding to common heat flux in a mild fire scenario. During this fire experiment, the peak heat release rate (pHRR), the total heat release (THR), and the time to ignition (TTI) were recorded as key parameters affecting the fire scenario. Typically, the cooccurrence of high pHRRs and low TTIs provides support for rapid ignition and fast fire propagation, which is detrimental. We also used *Flame-Retardancy Index* (*FRI*) as a universal dimensionless index enabling classification of polymer composites in terms of flame-retardancy performance as

Poor, *Good*, or *Excellent*.[22] Typically, due to the logarithmic transformation from *Poor* to *Good*, and then to *Excellent* class of flame retardancy based on which *FRI* categorizes polymer composites,[23] any promotion means a considerable change in the flame-retardancy performance.

UL-94 vertical flammability tests were conducted on the FIRE apparatus following the standard protocol outlined in ISBN 0-7629-0082-2. Five specimens, each measuring 125 × 13 × 3 mm^3, were cut from 150 × 100 × 3 mm^3 plates and exposed to two flame applications lasting 10 s each. The afterflame and afterglow durations were recorded along with any ignition of cotton caused by flaming particle drips. Based on defined criteria (Table 1), the UL-94 test results classified the samples as V_0, V_1, V_2, or no rating (NR).

The density of the smoke in the PP samples was determined according to the ASTM D2843 standard. The specimens (50 × 50 × 3 mm^3) were placed on a metal screen in a test chamber to burn under active flame conditions at 276 kPa pressure using a propane burner for 4 min. The measurements were based on the loss of light transmission through a volume of smoke collected under controlled, standardized burning conditions.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR) Spectroscopy. The chemical structure of TA is presented in Figure 2. FTIR spectra for TA and TA-P-K are shown in Figure 3. FTIR measurements were carried out to evidence the presence of the grafted phosphorus function and to highlight any modification of the TA chemical structure that could occur during its mechanochemical modification.

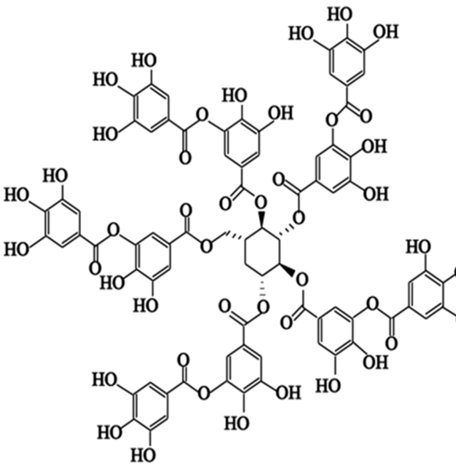

Figure 2. Simplified chemical structure of TA.

It is apparent from the FTIR spectra (Figure 3) that the spectra of TA and TA-P-K are very similar. Both show a strong absorption between 3700 and 3000 cm^{-1}, corresponding to the hydroxyl groups (OH) stretching vibrations and due to the wide variety of hydrogen bonding between OH. Peaks corresponding to C═O stretching and C−O vibration are observed at 1697 and 1313 cm^{-1}, respectively. In these spectra, we also note the presence of peaks corresponding to the deformation vibration of the carbon−carbon bonds in the phenolic groups in the region of 1500−1400 cm^{-1} and those related to the distortion vibration of C═C in benzene rings at 751 cm^{-1}.[24] Only one peak differs between the two spectra and appears at 509 cm^{-1} in the TA-P-K spectrum. This peak corresponds to the P−O bond and evidences the effective TA phosphorylation. It is important to notice that all of the other peaks related to TA appear in the TA-P-K spectrum in the same characteristic bands, indicating that the chemical structure of TA is preserved and not affected by the mechanochemical treatment, contrary to what we had already reported in our previous study,[12] which revealed the presence of gallic acid units, resulting from the hydrolysis of TA during its chemical modification by phosphorus chloride. This outcome looks very important, in view of demonstrating the advantage of the mechanochemistry method over solvent-based chemical processes requiring high temperatures and long reaction times that negatively affect the chemical structure of the additives. Such drawbacks are not the case when using mechanochemistry grounded on the bedrock of the ball-milling process, as proved in this study.

Thermal Degradation. In general, the thermal degradation of TA is affected by the nature of the atmosphere in which it occurs,[25] except for a small mass loss below 200 °C that was reported in both atmospheres and corresponded to the release of volatiles from TA in both cases. As per Figure 4, the major degradation of TA occurs at around 350 °C. Thermal decomposition of TA nitrogen results in an intumescent residue, while under air, it completely decomposes.[12] TA decomposition under nitrogen begins with a first dehydration stage up to 150 °C. The major degradation of TA occurs at 230 °C, leading to the production of chemical species like

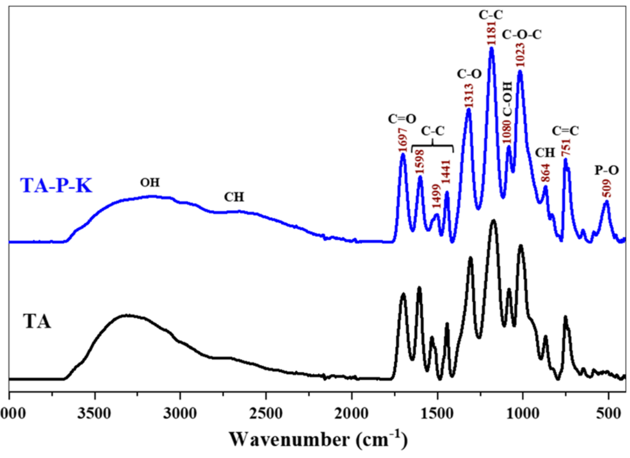

Figure 3. FTIR spectra of TA and TA-P-K modified and used in this study.

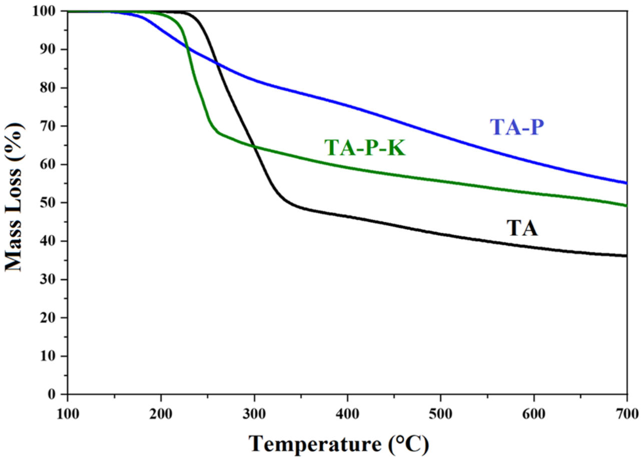

Figure 4. TGA curves of TA, TA-P, and TA-P-K under nitrogen at 10 °C·min^{-1}.

1,2,3-benzene triol and carbon dioxide, resulting from the disintegration of TA molecules initiated by decarboxylation of the outermost layer of gallic acid units.[25] At this stage, the inner layer containing the core units linked to the core glucose molecules remains intact and starts degrading only above 400 °C.

The chemical modification of TA through phosphorylation and potassium salt formation modified its thermal behavior. Figure 4 compares the TGA curves for TA and its derivatives (TA-P and TA-P-K). Notably, all products demonstrated important char-forming ability since the residue at 700 °C was >35% (Table 2). Although the shapes of the TGA curves of TA and TA-P-K remained unchanged, chemical modification induced some premature thermal degradation, as indicated by a shift in the TGA curve toward lower temperatures. In fact, the degradation temperature at the early stage of decomposition ($T_{-5\%}$) decreased from 242 °C for TA to 222 °C for TA-P-K. Furthermore, the addition of potassium phosphate groups improved the TA char-forming ability, considering that the amount of residue at 700 °C increased from 36 to 49% after modification (Table 2). These results are in decent agreement with already reported data in the literature, namely, that phosphorylation of TA causes a decrease in its thermal stability coupled with an increase in its charring ability.[12] It is also highly relevant to compare the behavior of TA-P-K with that of the TA-P_2O_5 mixture before precipitation (TA-P), which contains a much greater phosphorus content (7.55 wt %). Both products undergo premature thermal degradation, but the rate of mass loss is lower for TA-P even if its thermal degradation starts at a lower temperature ($T_{-5\%}$ = 200 °C). However, the amounts of the final residues are slightly similar for both additives, i.e., 55% for TA-P and 49% for TA-P-K.

Table 2. TGA Parameters for TA and Its Derivatives Obtained from TGA Curves under a Nitrogen Atmosphere at 10 °C·min^{-1}[a]

sample code	$T_{-5\%}$	residue at 700 °C (wt %)	P content (wt %)	K content (wt %)
TA	242	36	0	0
TA-P	200	55	7 (added P_2O_5)	
TA-P-K	222	49	2.0 ± 0.1	7.6 ± 0.1

[a] P and K contents were determined by ICP on the TA-P-K product.

Unmodified and modified TAs were incorporated into PP at 30 wt %. First, it was crucial to ensure that TA-P-K was properly dispersed in the polymer as poor dispersion could limit the flame-retardant effect of the additive and thus reduce the final performance of the composite. SEM−EDX images of the cryo-fractured surfaces of the PP/TA-P-K composite are presented in Figure 5. The images show the presence of small particles uniformly distributed throughout the PP matrix and the absence of large aggregates and highlight the significant correspondence between the particle traces and the presence of the two P and K elements. Furthermore, these images indicate that unlike most reported cases, the potassium phosphate salt precipitation step performed in this study did not contribute to the formation of large particles. It is also important to mention that the descent dispersion of the additive was achieved without any previous particle surface treatment.

The presence of TA, whether chemically modified or not, induced a significant evolution in the thermal stability of PP (Figure 6). While the blank PP polymer degrades completely in a single step, the degradation of PP composites occurs in two stages, meaningfully starting at lower temperatures. The first stage would correspond to the degradation of TA and its derivatives, while the second stage could be attributed to the degradation of transmuted PP and the formation of the residue. The temperature at which thermal degradation begins is, therefore, governed by the thermal degradation of the TA derivative used. It starts at 200 °C for PP composites containing less thermally stable TA derivatives, i.e., TA-P

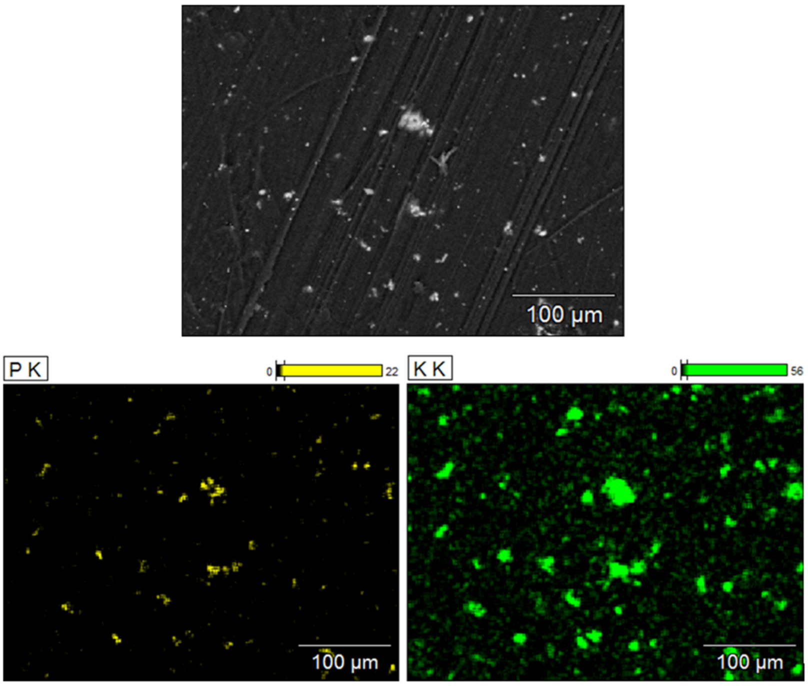

Figure 5. SEM−EDX images of the PP composite containing 30 wt % TA-P-K.

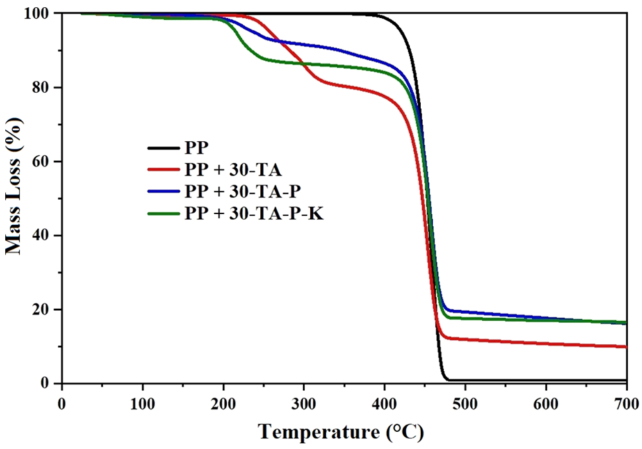

Figure 6. TGA curves of the pristine PP and PP composites containing 30 wt % TA and TA-P-K under nitrogen at 10 °C·min^{-1}.

and TA-P-K, while it begins at 230 °C in the presence of TA, and at 370 °C for unfilled PP. The decomposition temperatures at 5% ($T_{-5\%}$) follow the same trend (Table 3).

Table 3. TGA Parameters for All Composites Obtained from TGA Curves under a Nitrogen Atmosphere at 10 °C·min^{-1}

	$T_{-5\%}$	mass loss at 350 °C (wt %)	residue at 700 °C (wt %)
PP	420	0	0
PP-30TA	258	−20	10
PP+30TA-P	236	−10	16.5
PP- 30TA-P-K	215	−14	16.5

However, although PP+30TA-P and PP+30TA-P-K begin to degrade first, their first decomposition step is slower, leading to a much lower mass loss than that of PP+30TA. At 350 °C, for example, the mass loss recorded is −20, −14, and −10% for PP+30TA, PP+30TA-P-K, and PP+30TA-P, respectively. This could be ascribed to the difference in the mass loss of different TA derivatives alongside the formation of the charred residue, which limits the release of volatile products. Moreover, while neat PP decomposed completely, the final residue remaining at 700 °C was similar regardless of the nature of the modified TA (16.5 wt %), obviously more than for composite containing unmodified TA (10%).

Fire Behavior Analysis. Cone calorimetry is a reliable tool for assessing the fire behavior of polymers. It enables the obtention of the heat release rate (HRR) curve and the measurement of several parameters related to combustion, such as the TTI, pHRR, THR, and mass loss during combustion. To classify PP composites based on the flame-retardancy performance, cone calorimetry data can be considered to calculate *FRI*. A comprehensive review on the classification of PP composites based on flame-retardancy performance by *FRI* demonstrated that expecting *Excellent* flame retardancy from PP composites would be ambitious.[26] The review showed that even the combination or hybridization of phosphorus FRs with complementary additives at high loadings can hardly lead to such a class of flame retardancy. It was also unraveled assessing a huge pool of data on cone calorimetry analysis of PP composites that PP composites mostly take the *Good* label, differing in values in that interval under the influence of the type, amount, and hybridization of FRs. Conversely, for phosphorus-containing PP composites, the literature analysis was indicative of a high likelihood of having very high limiting oxygen index (LOI) values, for the majority of data by varying the *FRI* value in between 2 and 5 (*Good* region).

The HRR curves for PP and its composites containing TA and different TA derivatives are compared in Figure 7. The key parameters of the fire retardancy of the PP composites as well as calculated *FRI* values were extracted and are given in Table 4. According to the *FRI* values, all PP composites are categorized as *Good* with higher values for composites containing TA-P-K FR. This outcome should be considered promising bearing in mind the aforementioned discussion about the flame-retardancy label of the majority of flame-retardant PP composites reported in the literature but more pronounced considering that FRs developed in this study are sustainable. It may be obvious from the data that the PP selected for this study burns quickly, featuring a sharp pHRR of 730 kW m^{-2}. This is the characteristic of noncharring polymers defined in a reliable paper.[27] It is also noteworthy considering that the incorporation of unmodified TA induced some modification of the HRR curve, leading to a moderate yet significant reduction in the value of pHRR (−29.5%), down to 515 kW·m^{-2} and to the presence of some plateau around this value. This could be due to the natural ability of TA to form char, which was, unfortunately, not sufficient to achieve very low pHRR levels.

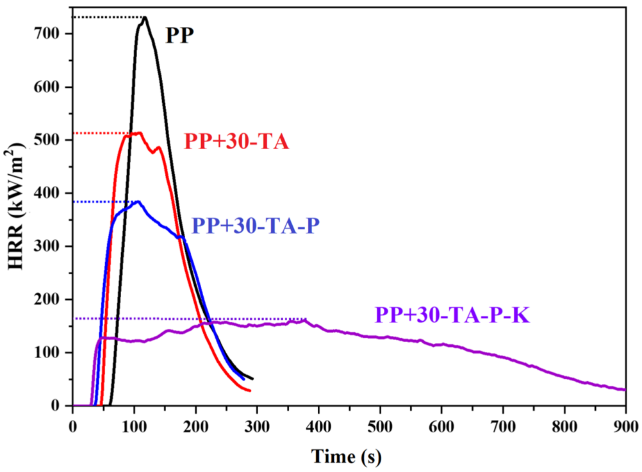

Figure 7. HRR curves obtained from the mass loss cone calorimeter test at 35 kW·m^{-2}.

Table 4. Results of the Mass Loss Cone Calorimeter Test (35 kW·m^{-2})

sample codes	TTI (s)	pHRR (kW·m^{-2})	THR (MJ·m^{-2})	pHRR reduction (%)	*FRI* (—)	*UL-94*
PP	60	730	74.1		—	NR
PP+30TA	48	515	68.0	−29.5	1.24	NR
PP+30TA-P	36	385	62.2	−47.3	1.36	NR
PP+30TA-P-K	28	160	101.0	−78	1.56	NR

The incorporation of TA also induced a decrease in the composite resistance to ignition since the TTI decreased from 60 to 48 s for pristine PP and composites with 30 wt % TA, respectively. This effect could be inferred by considering a range of possibilities. The incorporation of an additive that degrades more rapidly than the polymeric matrix led to a reduction in the thermal stability of the composite, as shown by TGA analyses (Figure 6). Indeed, the temperature corresponding to 5% mass loss ($T_{-5\%}$) decreased from 420 °C for PP to 258 °C in the presence of TA (Table 3). In addition, TA is a product that ignites relatively quickly since its ignition time during MLC testing at 35 kW·m^{-2} is estimated to be 20 s.[12]

Increasing the amount of char formed during TA thermal decomposition and its thermal stability is therefore necessary to enhance its flame-retardant properties. Our previous study demonstrated this by combining TA with different coadditives (nanoparticles, phosphorus-containing flame retardants) and by phosphorylating it.[12] Using phosphorylated TA proved to be highly effective in the cone calorimeter test. A very stable char was formed with a significant reduction in the pHRR for PLA containing 20 wt % phosphorylated TA.

A solid-phase process rather than a liquid-phase process was used in the current study to modify TA and obtain a potassium/phosphate TA derivative (TA-P-K) containing 2.0 wt % P and 7.0 wt % K with a reaction yield of 87%. The incorporation of 30 wt % TA-P-K into PP enabled a very low pHRR value (160 kW·m^{-2}) to be reached during the MLC test, corresponding to a large pHRR reduction of approximately −78% (Figure 7 and Table 4). In comparison, the MLC test of the PP composite containing the same content of nonpurified phosphorylated TA (TA-P) (which contained a much greater phosphorus content, i.e., 7.55 wt %) demonstrated a significant pHRR reduction but was much lower than that obtained using TA-P-K. In fact, the pHRR reduction reached with PP+30TA-P was limited to −47.3% (pHRR = 385 kW·m^{-2}). Thus, converting phosphorylated tannic acid (TA-P) into its potassium phosphate salt form (TA-P-K) significantly improved its flame-retardant performance.

However, the sharp decrease in the pHRR was accompanied by a decrease in the ignition time. TTI was approximately 36 s in the presence of TA-P and 28 s in the presence of TA-P-K. This decrease could be explained by (1) the reduced thermal stability of TA derivatives, as already detected through TGA analyses (Figures 4 and 6), and by (2) the brown/black color of the composite containing TA derivatives, which could modify the heat absorption of the composite. This leads to a faster increase in the temperature at the surface of the tested plate. An increase in the heat absorption of the material due to its coloration promotes ignition by inducing stronger heating of the decomposition gases. This behavior was already suggested by others to explain the reduction in TTI in acrylonitrile butadiene styrene (ABS) and PLA containing dark lignin.[28,29]

The very sharp reduction in the pHRR was achieved due to the modification of the residue shape/structure, which was induced by the combination of phosphorus and potassium. Indeed, whereas the combustion of PP alone or containing TA and even TA-P leads only, at the end of the MLC test, to a noncohesive char, if any, the combustion of the composite containing TA-P-K stands out for its expanded intumescent form (Figure 8). The formation of this layer reduces the level of combustion by preventing volatiles from entering the combustion zone. This is demonstrated by the mass loss curves presented in Figure 9, which shows that the mass loss rate of the PP + 30TA-P-K composite is greatly reduced, and the composite decomposes for 900 s, whereas the other blends decompose completely in less than 300 s. Combining phosphorus with potassium significantly improves the flame-retardant efficiency of TA-P by promoting (1) the formation of a large quantity of char, (2) its expansion during combustion, and (3) improving its resistance to thermal degradation.

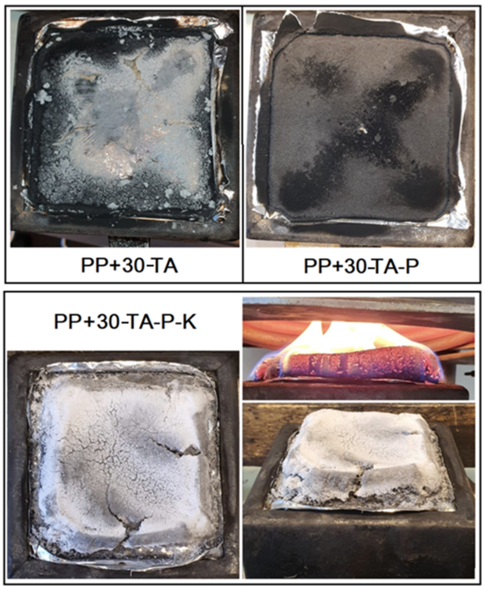

Figure 8. Photos of char residues of different PP composites containing TA, TA-P, and TA-P-K additives after the cone calorimeter test (35 kW·m^{-2}).

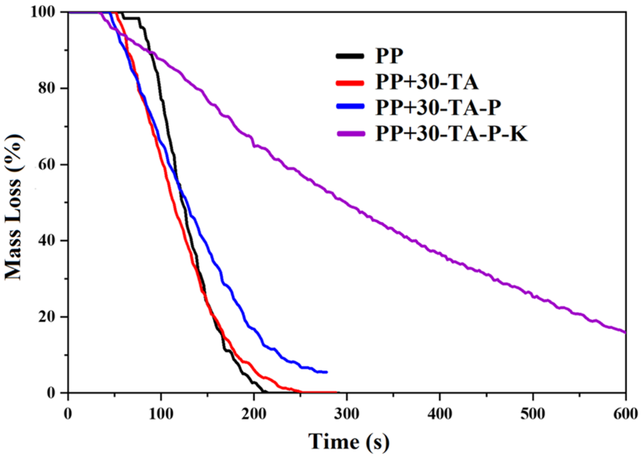

Figure 9. Mass loss curves of PP and its composites containing TA, TA-P, and TA-P-K additives (35 kW·m^{-2}).

It is also important to note the large difference between the thermal stabilities of the composites measured by TGA and those measured during MLC testing. According to TGA measurements, the PP+30TA-P-K composite did not show a thermal stability significantly higher than that of the other two composites, while MLC tests showed that this composite has much greater thermal stability. This difference also reminds us how difficult it is to use data obtained on a few milligrams test scale to predict the macroscopic thermal behavior of a material. Relationships between laboratory-scale TGA results and pilot cone calorimeter test in which different physical effects such as mass or heat transfer barriers occur, are not obvious at all and should be established with great caution.

Figure 10. Images of PP composite samples exposed to a gas burner during the smoke density test.

The precipitation of TA-P, obtained by ball-milling chemistry, seems to be therefore an effective route for (1) recovering water-insoluble TA salt and (2) boosting its performance as a flame retardant in PP. The superior flame-retardant effect observed in the presence of TA-P-K is due to the well-known synergy between phosphorus and metals, although potassium is not widely used in this application. The combination of P and the metal promotes the formation of thermally resistant metal phosphate structures. This combination could either be achieved by combining phosphorus compounds with metallic additives such as oxides[30−33] or by forming metal phosphate salts,[34] as in the current study.

Despite the significant improvement in flame retardancy observed in cone calorimetry tests, the incorporation of modified TA failed to enhance the material's classification in the UL-94 vertical burning test, which remains with no rating (NR) (Table 4). The material does not self-extinguish after ignition and continues to burn, forming dripping particles that ignite the cotton. This demonstrates that TA-P-K is highly effective in reducing the pHRR during MLC testing in a horizontal position, where there is no material dripping. However, in a vertical position, the ignited material drips and causes the cotton to ignite. Therefore, it can be concluded that TA-P-K should be combined with other flame retardants to minimize dripping and enhance its fire classification in the UL-94 test while preserving a low pHRR value.

Smoke generation during combustion is also a critical element of fire safety. This issue needs to be considered when developing and fine-tuning flame-retardant systems. In fact, flame retardants aim to disrupt the fire triangle and hinder combustion. This often results in incomplete combustion, generating more smoke than when the polymer burns alone.

Neat PP and its composites containing 30 wt % TA and TA-P-K were tested for smoke opacity in accordance with ASTM D2843. The test procedure is illustrated in Figure 10, while the results are shown in Figure 11. Since the test was carried out under burning conditions, smoke opacity might also be affected by the presence or absence of intense flames. This partially explains the shape of the curve for PP alone. In fact, at the initial stage when the flame contacted the plate, smoke is released, causing the chamber to become opaque. However, this parameter decreases after 36 s as a result of plate ignition, which generates a large flame inside the chamber, consuming part of the accumulated smoke, thereby reducing the overall opacity. Finally, the opacity value increases again because of the smoke produced during polymer combustion but decreases later due to the flow of material that is no longer in contact with the burner, causing combustion to stop. A similar behavior was observed during the test of the PP composite containing TA. The light absorptivity decreased after the ignition of the gases released (first peak) but then increased until the chamber is saturated. As the material produced some char during its decomposition, it remained in contact with the flame and continued to burn/degrade. On the other hand, the

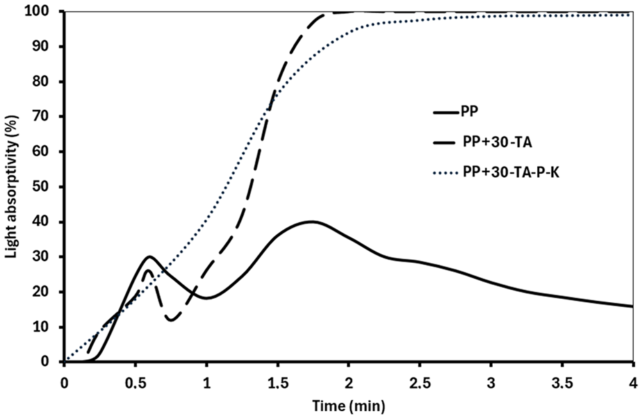

Figure 11. Light absorptivity curves of the neat PP and its composites containing 30 wt % TA and TA-P-K during the smoke density test.

composite containing TA-P-K did not ignite and formed a charred residue on the surface of the exposed plate, which contributed to the increase in smoke production. These results highlight the complexity of developing new flame-retardant systems, which generally require the combination of several additives, including smoke suppressants such as metal oxides.[35]

CONCLUSIONS

An innovative chemical modification process based on mechanochemistry was applied in developing a sustainable biobased FR for PP. TA, as a biobased, low-cost starting raw material, was selected for its char-forming ability during thermal degradation. It was chemically modified by grafting potassium phosphate moieties under mild process conditions. First, the reaction step with P_2O_5 was carried out by ball-milling for 1 h, followed by a precipitation step in the aqueous phase with KOH. A TA-P-K derivative containing 2.0 wt % phosphorus and 7.6% potassium with enhanced char-forming ability was obtained. Taking the label of *Good* based on *FRI* calculation, its incorporation at 30 wt % into the PP matrix significantly enhanced the fire retardancy of PP, with a pHRR reduction of 78%. The superior flame-retardancy result obtained with TA-P-K during the MLC test was attributed to the synergistic metal/phosphorus effect that was responsible for the formation of an intumescent char during combustion. However, the composites containing modified TA failed to achieve any classification in the UL-94 test, highlighting the necessity of developing synergistic combinations with other FRs to achieve a V_0 classification. Moreover, smoke opacity increased during smoke tests, indicating that the used additive needs to be combined with smoke suppressant agents, which were classically used with phosphorus FRs in industrial formulations. The chemical modification used in this research provides new opportunities for the development of TA biobased FRs and opens new prospects to upgrade other low-cost additives such as lignin or cellulose in technical applications using environmentally friendly mechanochemistry processes.

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ABBREVIATIONS

TA, tannic acid; FR, flame retardant; FRI, flame-retardancy index; PLA, polylactide; LFPN, lignocellulosic-based P-N; TA-P-K, potassium phosphate tannic acid; TGA, thermogravimetric analysis; ICP, inductively coupled plasma analysis; FTIR, Fourier transform infrared; PP, polypropylene; TA-P, phosphorylated TA; SEM−EDX, scanning electron microscopy−energy dispersive X-ray; MLC, mass loss cone calorimeter; pHRR, peak of heat release rate; THR, total heat release; TTI, time to ignition; HRR, heat release rate

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