

Effective Phosphorus/Phosphorus-Nitrogen Fire Retardants Applied to Biocomposites Based on Polypropylene-Wood Flour: Flammability, Thermal Behavior, and Mechanical Properties

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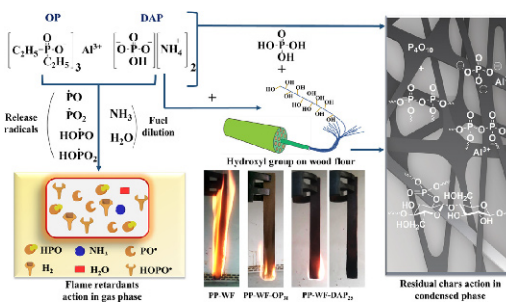
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Abstract: By adding diammonium phosphate (DAP) or aluminum diethyl phosphinate (OP) as flame retardants, flame retardancy of composites based on polypropylene and wood flour (PP-WF) improved significantly. A loading of 25 wt% DAP achieved a UL-94 V-0 rating as well as LOI value of 29%, which increased by 52.6% compared with that of the PP-WF composite alone. A 30 wt% OP loading provided a rating of UL-94 HB standard, and achieved LOI value of 28%. Meanwhile, the PP-WF composite without flame retardant, completely burned to the sample holder clamp with low LOI value (19%). Thermal properties of the PP-WF composite with and without DAP and OP flame retardants, were investigated using TGA and DSC. Flame retardant performance was also studied, through the morphology and chemical structure of residual char by TGA, FTIR, SEM, and XPS analyses. There was interaction between DAP and the composite, which played a key role in maintaining mechanical properties of the material.

Keywords: polypropylene/wood flour composite, polymer composite flame retardancy, thermal stability, phosphorus/phosphorus-nitrogen flame retardant, fire retardant performance.



1. Introduction

Natural wood-flour reinforced polymer composite materials are better known as a form of a well-known form of wood plastic composite (WPC), which is a type of biocomposite that is environmentally friendly and widely used in many fields, especially in transportation, consumer products, the construction industry, and in outdoor products and other applications.¹⁻⁶ Among the polymers used, polypropylene (PP) has been more widely used in the manufacture of WPC because it has more advantages than polyethylene and polyvinyl chloride. Polypropylene-wood flour (PP-WF) composite, referred to as PP-WF composite, has the advantages of plastic such as being easy to shape, having a variety of colors, and being fungus and insect resistant in comparison with wood products while making use of the excess wood flour from other industries.

However, apart from the superior properties of biocomposites due to the favorable performance of both WF and PP, combinations of PP and wood flour exhibit high flammability, and this is the primary drawback of using PP-WF composites. One well-known way to improve the fire-resistance of the polymer

composite is to add halogen flame retardant additives. For environmental protection concerns and limiting negative effects on human health, halogen-free flame retardants (metal hydroxides, nitrogen and/or phosphorus compounds as well as intumescent flame retardant (IFR), etc.) have been studied extensively in recent years. IFR is one of the most widely used systems because of its effective flame retardancy and its production of less smoke during combustion, but it is sensitive to moisture, leading to limitations in its applications.⁷ Another flame retardant (FR) is metallic hydroxide, a good fire-proof additive for WPC *via* the mechanisms of dilution and cooling. However, it also has the disadvantage of requiring the use of large quantities to improve fire retardancy, which negatively affects the processing and mechanical properties of WPC. Phosphorus and phosphorus-nitrogen compounds are not only environmentally friendly but also highly effective against fire, and the fire retardancy of substances such as ammonium polyphosphate and melamine polyphosphate have recently been discussed.⁸⁻¹⁶

Some of the above studies have examined the flame retardancy of phosphorus and phosphorus-nitrogen FRs when applied to WPC. However, no studies have been performed on the flame retardant behaviors and thermal properties of other phosphorus compounds, such as diammonium phosphate (DAP) or aluminum diethyl phosphinate (OP), for WPC based on PP, although their high fire retardancy has been reported for other polymers and polymer composites.^{17,18} OP has been reported to

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improve the flame retardancy of unsaturated polyester (UP); the UL-94 V-0 rating has been obtained, and the LOI value increases from 21 to 29.5% with 25 wt% OP loading for UP from virgin chemical mixtures.¹⁸ Furthermore, for UP derived from recycled poly(ethylene terephthalate), the presence of DAP or OP significantly improves the flame retardancy and thermal stability; the LOI value increases from 20 to 28%, and the V-0 rating is achieved at a relatively low loading of 8 wt% DAP or 10 wt% for OP.¹⁷ More recently, DAP has been used as a flame retardant for wood flour/expanded polystyrene waste composites¹⁹ and for polyvinyl chloride/wood flour.²⁰ It was indicated that there is a good interaction between DAP and WF, and DAP is efficient at improving the limiting oxygen index and increasing the flame retardancy and thermal properties of composites.

Generally, nonhalogenated FRs used for PP or PP-WF composites with current phosphorus and/or phosphorus-nitrogen compounds are inefficient at obtaining UL-94 V-0 ratings without needing to be added in relatively large quantities. Normally, FRs are incorporated into polymers or polymer composite materials additively; there is almost no chemical means, so high FR loading restricts the mechanical properties and processability of composites. The heteroatoms of cellulose and aromatic rings of lignin play a role as residual char layers,^{6,21} and no charring agent seems to be necessary to flame retard WPC. However, without additional charring agents, the fire retarding performance of PP-WF composites is not adequate. As mentioned, DAP is safe, inexpensive, and has a high phosphorus content, is an effective flame retardant at even low loading, and has good interaction with WF.^{19,20,22-24} DAP and OP also leave high residual char, protecting composites from fire. These materials may provide an increase in flame retardancy with little reduction in mechanical properties. Therefore, the objective of this study is to investigate the effects of DAP and OP flame retardants on the flame retardancy, mechanical, and thermal properties of PP-WF composites. The degradation behavior, the interaction between FR and composite, and the chemical composition and morphology characterization of the residual char are also discussed.

2. Experimental

2.1. Materials

Polypropylene (PP - PP 1102K) was supplied by Thailand Polimaxx. Wood flour (WF - E 35) with a mesh size ranging from 50 to 80 was purchased from La Sole Est Srl Company. Diammonium hydrogen phosphate (DAP) was purchased from Guangdong Guanghua Chemical Factory Co., Ltd. Aluminum diethyl phosphinate (OP - Exolit OP 1240) was obtained from Clariant.

2.2. Compounding and processing the composites

Wood flour was washed with warm water to remove impurities and then dried in an oven at 70 °C to constant weight. The mixtures (Table 1) were added to a high intensity mixer for 3 min and then mixed in a Haake PolyDrive two-screw extruder at 170 °C, the screw speed was 50 rpm for a mixing time of 5 min. After that, the PP-WF composites were converted to standard

Table 1. Main formulation of PP-WF and PP-WF/FR composites (by wt%)

Samples	PP-WF ^a	DAP	OP
PP-WF	100	0	0
PP-WF/DAP ₂₀	80	20	0
PP-WF/DAP ₂₅	75	25	0
PP-WF/OP ₃₀	70	0	30

^aPP-WF: 50-50 (wt-wt).

sheets by hot-forming at 170 °C for 7 min, and the forming bars were obtained and used for further analyses.

2.3. Characterization and measurements of the composites

2.3.1. Flame retardancy

Fire retardant properties were determined by the limiting oxygen index (LOI) test (Qualitest, USA) according to ASTM D 2863 and UL-94 according to the testing procedure of FMVSS 302/ZSO 3975. Five specimens for each composite material were sampled, five test bars of 127×12.7×3.0 mm³ of each specimen were tested for UL-94, and five test bars of 100×10×3 mm³ of each specimen were tested for LOI.

2.3.2. Thermal analysis

Thermogravimetric analyses (TGA) were performed on 2 to 10 mg samples under an air atmosphere at a heating rate of 20 °C/min using a TGA 2050 thermogravimetric analyzer. The temperature range was from 50 to 700 °C.

Differential scanning calorimeter tests (DSC) were carried out on a TA 2910 DSC instrument under a flow of N₂ gas. The samples were heated from -50 to 200 °C at a heating rate of 20 °C/min and cooled from 200 to -50 °C at a cooling rate of 10 °C/min. Then, the samples were heated from -50 to 200 °C at a heating rate of 10 °C/min.

2.3.3. Spectroscopic analysis

Fourier transform infrared spectra (FTIR) were measured by a Thermo Scientific Nicolet 380 FT-IR Spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS HSI spectrometer using a monochromatized Al K α X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms (40 eV energy). The anode voltage and current were set to 15 kV and 10 mA, respectively.

2.3.4. Field emission scanning electron microscope

The outer surface morphology of residual char was studied via FE-SEM (JEOL JSM - 7401F, Japan) at an acceleration voltage of 15 kV. The specimens were sputter-coated with a conductive layer of platinum prior to analysis.

2.3.5. Mechanical testing

Five specimens of each composite were measured for their flexural modulus and flexural strength on a Universal Testing Machine AG-X plus Shimadzu according to ASTM D790-00. An unnotched Charpy impact strength test was carried out on a Zwick HIT25P Shimadzu according to ISO 179-1/1eU using a Ceast Resil Impact tester with hammer energy of 5 J for each sample.

3. Results and discussion

3.1. Flame retardancy

Combining polypropylene with wood flour has a negative impact in the form of a strong increase in flammability. UL-94 and LOI, which are well-known, simple and precise methods for the determination of fire self-extinguishment, were used to evaluate the flame retardancy of PP-WF and PP-WF/FR composites. UL-94 tests of the composites were investigated through horizontal and vertical burning (UL-94 HB and UL-94 V), and the results are shown in Table 2. In the absence of FR, the PP-WF composite completely burns to the sample holder clamp with a low LOI value of 19%. In the presence of DAP or OP, the flame retardancy of the PP-WF composite is improved significantly. The addition of 20 wt% of DAP or 30 wt% of OP does not achieve the rating of UL-94 V, but it does increase the fire performance of the PP-WF composite to the UL-94 HB rating level. Normally, a loading of 30 wt% FR or more is required to provide effective self-extinguishing properties to thermoplastics such as polyolefins. Nevertheless, in this study, a loading of 25 wt% DAP can achieve a UL-94 V-0 rating. In the temperature range of 150–600 °C, DAP decomposes to ammonia, water, and phosphoric acid, which can be further dehydrated, producing phosphorus-containing and/or forming P_4O_{10} (or P_2O_5) layers.^{24–26} These layers could function as a barrier layer for heat and oxygen transport, while the release of NH_3 and H_2O could induce flame inhibition due to the cooling effect and fuel dilution of the oxygen and fuel gases during combustion.

OP decomposes at high temperature, and the flame retardant mechanism of OP is expected to act in both phases. With the vapor phase, diethylphosphinic acid is released from OP during combustion and then vaporized to the gas phase, yielding active radicals^{27–31} that act as scavengers for H^* and OH^* . In the condensed phase, phosphinic/phosphoric acid and/or phosphorus-containing moieties, which are the pyrolysis products of OP, self-condense or react with other products generated from the decomposing PP-WF to form a stable charred residue, reducing the generation of volatilized products of combustion and protecting the PP-WF composite from the transfer of fire, flammable gases, and heat.

The LOI value increases from 18 to 29% with the loading of 25 wt% of DAP and this value is 28% with the loading of 30 wt% of OP. This confirms that higher oxygen content is required to initiate and sustain combustion of the materials in the presence of FR. The UL-94 and LOI results indicate that DAP and OP are effective flame retardants for PP-WF composites.

3.2. Thermal properties

3.2.1. Thermogravimetric analysis (TGA)

Figure 1 and Table 3 show the values T_{10} , T_{50} , T_{80} (the temperatures at which 10, 50, and 80% mass loss occur, respectively) and the residual char at 500–600 °C, along with the TGA data of PP-WF composites with and without flame retardant additives from 50 to 700 °C at a heating rate of 20 °C/min under an air atmosphere. According to the TGA curve of the PP-WF composite, only one main mass loss step of thermal decomposition is observed in the temperature range of 279–415 °C, and very little residual char is left at 600 °C (1.4 wt%). The TGA curve of the PP-WF/30 wt% OP composite shifting to high temperature displays one-step decomposition from 304 to 470 °C and leaves a higher charred residue (21.8 wt%) than that of PP-WF (1.4 wt%). OP decomposes at high temperature, which begins at 340 °C and leaves significant residual char of approximately 30.9 wt%. The char layer reduces the combustion rate of the composite material,

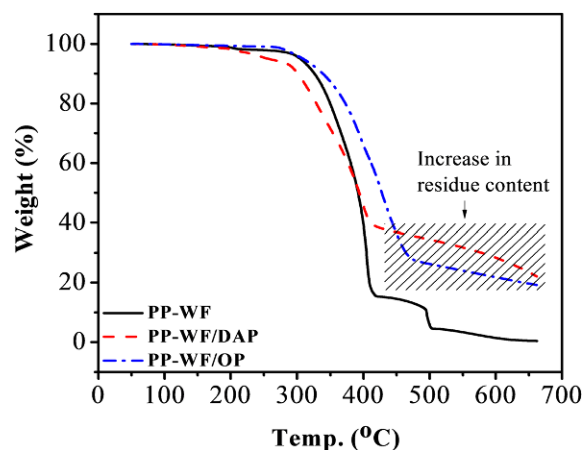


Figure 1. TGA curves of PP-WF, PP-WF/OP, and PP-WF/DAP in air.

Table 2. UL-94 results for PP-WF and for the mixtures of PP-WF with FR

FR	Samples	PP-WF/FR (wt/wt)	UL-94 Rating	
			UL-94 V	UL-94 HB
	PP-WF	100.0/0.0	No rating	burn to the sample holder clamp
DAP	PP-WF/DAP ₂₀	80.0/20.0	No rating	stop to burn before 25 mm mark
	PP-WF/DAP ₂₅	75.0/25.0	V-0	stop to burn before 25 mm mark
OP	PP-WF/OP ₃₀	70.0/30.0	No rating	stop to burn before 25 mm mark

Table 3. Thermal stability parameters

Samples	PP-WF/FR (wt/wt)	T_{10} (°C)	T_{50} (°C)	T_{80} (°C)	Residual char (%)	
					500 °C	600 °C
PP-WF	100.0/0.0	325.8	391.7	409.0	5.7	1.4
PP-WF/DAP ₂₅	75.0/25.0	300.9	393.7	666.0	34.4	28.4
PP-WF/OP ₃₀	70.0/30.0	338.3	427.7	642.2	26.2	21.8

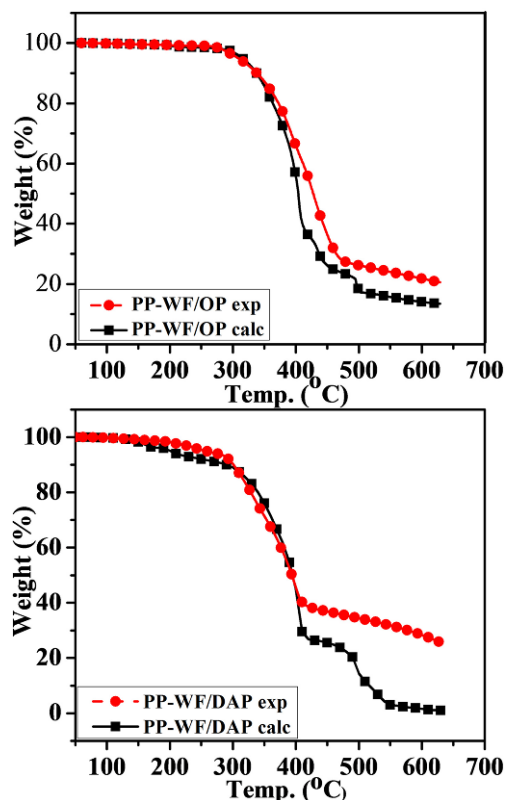


Figure 2. Experimental and calculated TGA values for PP-WF/OP and PP-WF/DAP.

and then, the thermal behavior of PP-WF/OP shifts to higher temperatures than that of PP-WF. The maximum temperature of the main decomposition step of PP-WF is 415 °C, while that of PP-WF/OP is 475 °C.

The onset decomposition temperature of PP-WF/25 wt% DAP is 256 °C, which is lower than that of PP-WF. With the addition of 25 wt% DAP, the weight loss of PP-WF/DAP (60%) is far lower

than that of PP-WF (85%). This indicates that the addition of DAP increases the first-step decomposition of the PP-WF composite and consequently promotes char formation, protecting the underlying material from further degradation.

These results show that the thermal behavior of the PP-WF composite is notably improved in the presence of DAP or OP in the high temperature range. To investigate the interaction between the PP-WF composite and FRs, the calculated and experimental TGA curves of PP-WF composites containing flame retardant were studied (Figure 2). The calculated TGA value is determined according to the following formula:

$$M = \frac{F \times \text{wt\%FRs} + W \times (100 - \text{wt\%FRs})}{100} \quad (1)$$

where M is the calculated TGA value, F is the TGA value of the FR additive, and W is the TGA value of the PP-WF composite.

The maximum weight loss of PP-WF/FR composites in the experimental TGA curve is lower than that of PP-WF/FR composites in the calculated TGA. The residual amount of char of the calculated TGA curve (1.4% for PP-WF/DAP and 14% for PP-WF/OP) is significantly lower than that of the experimental data (28.3% for PP-WF/DAP and 22% for PP-WF/OP) at 600 °C. The improved char yield is probably caused by the esterification of the formed phosphoric acid or polyphosphoric acid during the decomposition of flame retardant additives with the primary hydroxyl groups of cellulose. Cellulose phosphate formation occurs then further heating crosslinked char structure is occurred. Thus the amount of char in condensed phase increases.^{19,32,33} This is the main reason for the char yield increase especially in the case of DAP. It can be concluded that there is an interaction between FR and/or the decomposition products of FR and PP-WF composite and/or the decomposition products of PP-WF that greatly promotes the formation of more thermally stable residual chars, which further explains the improvement in flame retardancy of PP-WF composite (Figure 3).

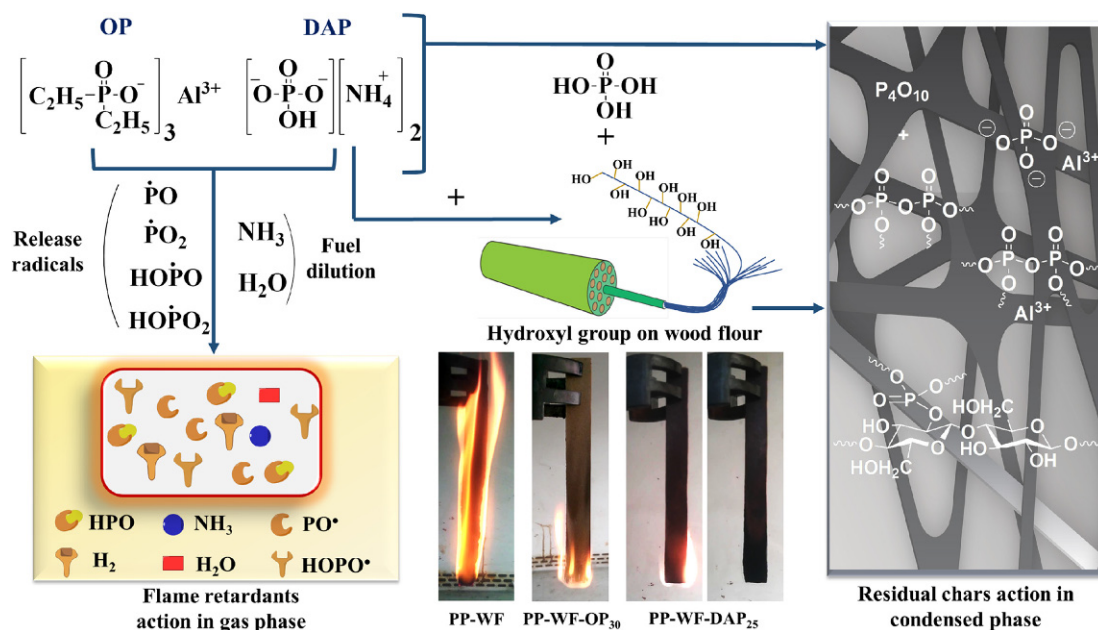


Figure 3. Schematic illustrations for the flame-retardant mode of action of PP-WF/FR and for the interaction between FRs and PP-WF (the reaction between phosphoric acid and primary hydroxyl groups during thermal decomposition is cited from literature¹⁹).

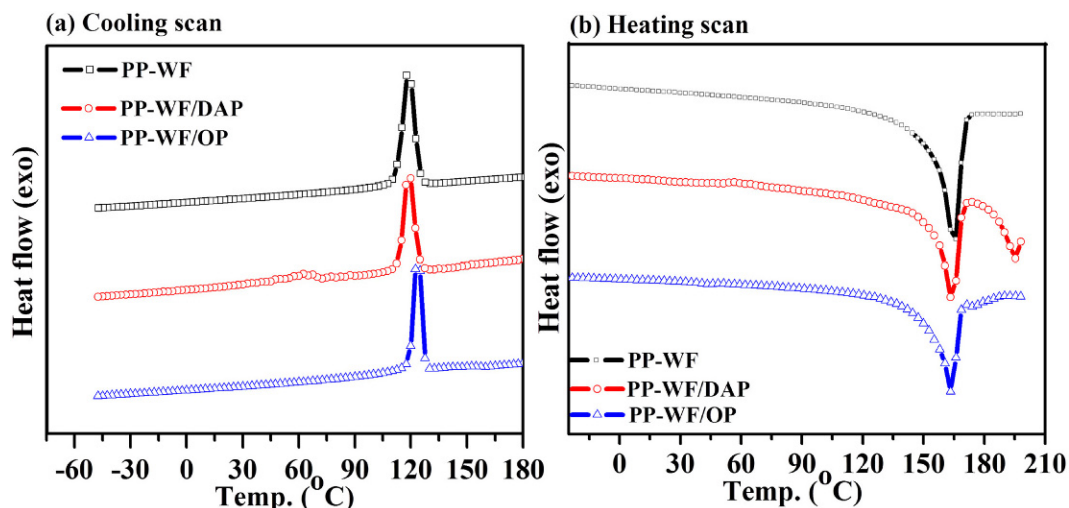


Figure 4. DSC results of PP-WF, PP-WF/OP, and PP-WF/DAP.

3.2.2. Differential scanning calorimetry analysis (DSC)

The thermoplastic properties of the composites were studied via DSC analysis (Figure 4); the melting temperature (T_m), the enthalpy (ΔH_m), the temperature of the crystallization (T_c), the crystalline enthalpy (ΔH_c), and the degree of crystallinity χ_c (%) are shown in Table 4. The results indicate that the addition of 25 wt% DAP or 30 wt% OP decreases the ΔH_m . The FR consumes more heat energy in the melting of the composite, so the ΔH_m of the PP-WF/FR is much lower than that of the PP-WF composite. The T_c increases to 119.3 °C for PP-WF/25 wt% DAP and to

124.3 °C for PP-WF/30 wt% OP. Meanwhile, this value for PP-WF is 118.7 °C. The crystalline enthalpy values of PP-WF/FRs are lower in comparison to those of PP-WF. Because the addition of flame retardant may obstruct crystallization, the decrease in ΔH_c was closely related to the decrease in the degree of crystallinity. χ_c (%) is generally affected by the amount of FR loading, the dispersion, and the viscosity of the mixture. As shown in Table 4, the crystallinity of the PP-WF composite is 49.84%. In the presence of FR, the χ_c (%) values of PP-WF/FR decrease (32.86% for PP-WF/25 wt% DAP and 46.03% for PP-WF/30 wt% OP).

Table 4. Melting and cooling parameters of PP-WF and of PP-WF/FR composites^a

Samples	Cooling scan		Heating scan		
	T_c (°C)	ΔH_c (J/g)	T_m (°C)	$-\Delta H_m$ (J/g)	χ_c (%)
PP-WF	118.7	49.82	164.9	51.59	49.84
PP-WF/DAP ₂₅	119.3	37.30	164.1	25.51	32.86
PP-WF/OP ₃₀	124.3	37.91	163.9	33.35	46.03

^a T_c is the temperature of the crystallization. T_m is the temperature of the melting. χ_c is crystalline; $\chi_c = \frac{\Delta H_m}{\Delta H_m^*} \times \frac{1}{W_{PP}}$. ΔH_m^* is the heat of melting of the fully crystalline PP (207 J/g). W_{PP} is the weight fraction of PP in the composites.

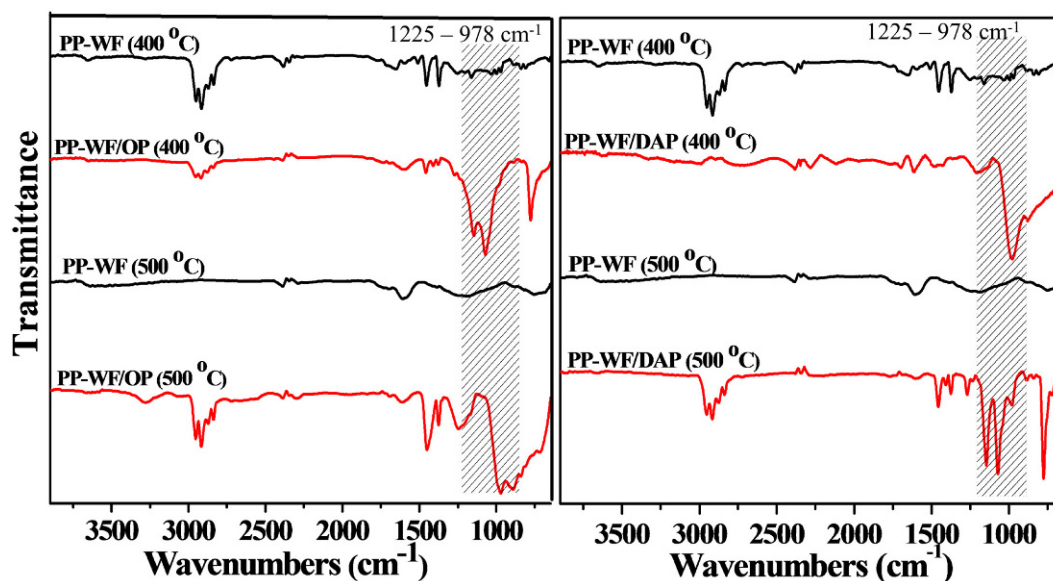


Figure 5. FTIR spectra of residual chars of PP-WF, PP-WF/OP, and PP-WF/DAP.

3.3. Chemical composition and morphology characterization of the residual char

To further study the effect of FR on the flame retardancy of the composite, analyses of condensed phases of PP-WF, PP-WF/DAP, and PP-WF/OP that were burned in a furnace at different temperatures are performed by FTIR, FE-SEM, and XPS. In comparison with the FTIR results for PP-WF residue, there are new bands

of P=O, P-O-C, and P-O-P appearing at 1225-978 cm^{-1} in the FTIR spectra of PP-WF/DAP and PP-WF/OP residual layers (Figure 5). The peaks at 775-850 cm^{-1} are attributed to aluminum phosphate and/or P-N groups. At 500 °C, a major part of the PP-WF composite has been volatilized, as indicated by a strong decrease in its characteristic absorptions. However, they still remain in the PP-WF/FR composites. This reveals that the formation of residual char containing phosphoric/polyphosphoric and/or their

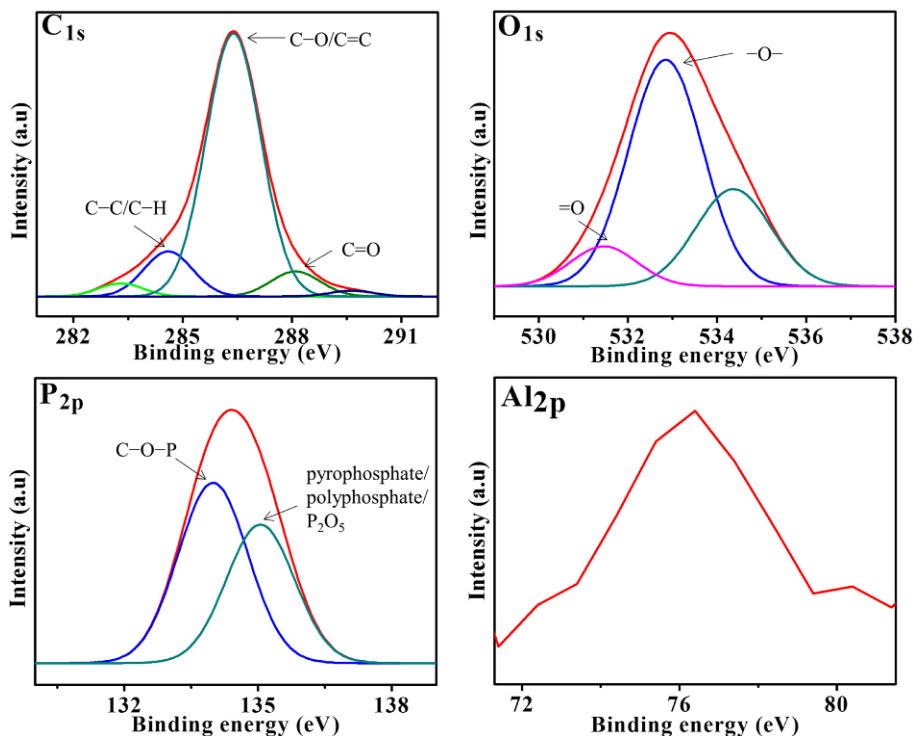


Figure 6. XPS spectra of residual chars of PP-WF/OP.

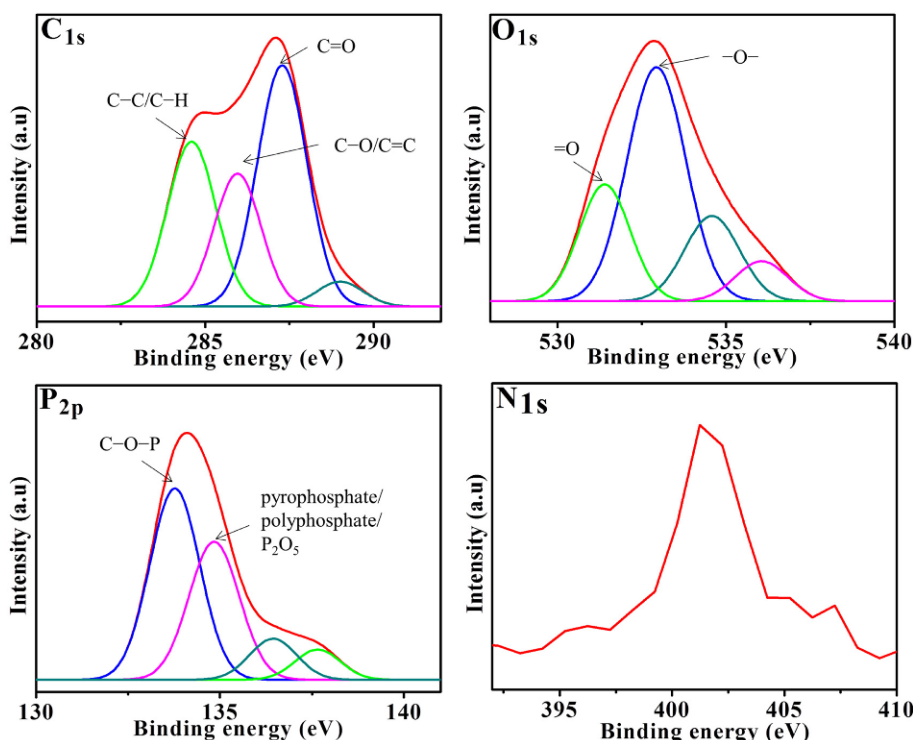


Figure 7. XPS spectra of residual chars of PP-WF/DAP.

derivatives acts as a barrier protecting the polymer from fire. These results fit very well with the experimental TGA results. The TGA curves of PP-WF/DAP and PP-WF/OP show residual char (500-600 °C) playing a role as a heat-stable barrier preventing the combustion of a composite that contacts a heat source and flammable gases, so that the presence of DAP or OP contributes markedly to the flame resistance properties of PP-WF composites.

The XPS results given in Figure 6 and Figure 7 show the chemical composition of the char residue of PP-WF/FR. The peaks at 284-288 eV are attributed to C_{1s}. The C_{1s} spectra reveal peaks that could be attributed to the contribution of C-C, C-H, C-O, C=C, C-O-P, and C=O. The O_{1s} spectra (531-536 eV) feature peaks that could be ascribed to O=C, O=P, and -O- in the C-O-C, C-O-P, -COO-, and/or C-OH groups. The peaks at 133.8-135.5 eV correspond to P_{2p}. The peaks in the P_{2p} spectra could be attributed to P-N, P-O-C, and/or PO₃⁻ groups in pyrophosphate and/or polyphosphate and/or P₂O₅. The Al_{2p} spectrum (76.4 eV) corresponds to aluminum phosphate. The binding energy of approx-

imately 399.4-404.2 eV can be attributed to N_{1s}. This implies that phosphorus-nitrogen-containing moieties remain in the charred layer.

The SEM results indicate the formation of a heat-resistant residual char containing phosphorus moieties during the thermal degradation of PP-WF/FR composites. This increases the density, compactness, and continuity of char layers (Figure 8) and, inversely, decreases the porosity and holes in the residual char of virgin PP-WF caused by poor char formation or less condensed char during combustion. The compact and continuous char layer of PP-WF/FR as acts as a protective barrier that could prevent the transfer of mass and heat in the solid phase during combustion.

3.4. Mechanical properties of composites

Figure 9 and Table 5 describe the flexural properties and impact strength of PP-WF and PP-WF/FR composites. The effect of additive-type fire retardants on the mechanical properties of composite materials is a matter of concern. Especially for high loading levels of FR (30 wt% OP), the interaction of the polymer matrix and filler has less compatibility, and the composite could lead to breakage. Then, the flexural strength of PP-WF/OP signifi-

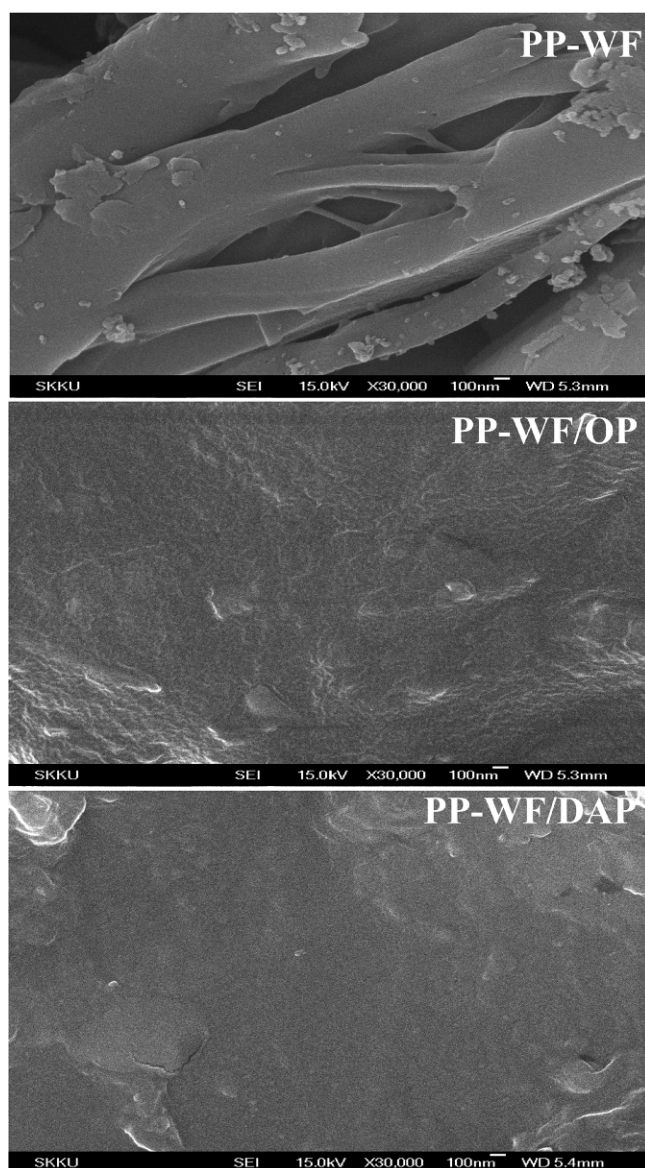


Figure 8. Surface morphology of residual chars of PP-WF, PP-WF/OP, and PP-WF/DAP analyzed via FE-SEM.

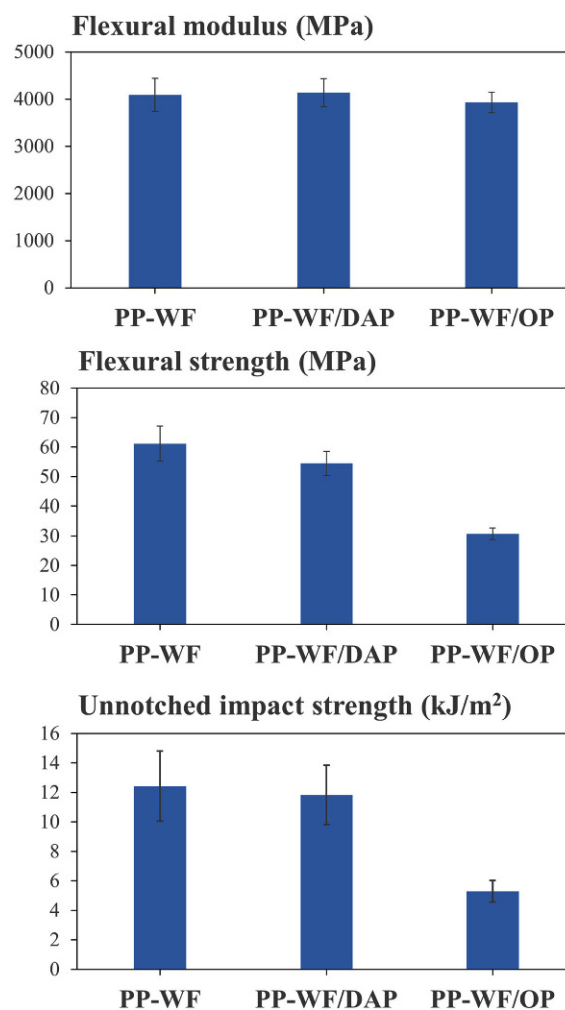


Figure 9. Mechanical properties of PP-WF, PP-WF/OP, and PP-WF/DAP.

Table 5. Mechanical properties of PP-WF and of PP-WF/FR composites

Samples	Flexural modulus (MPa)	Flexural strength (MPa)	Impact strength (kJ/m ²)
PP-WF	4094.2 ± 351.7	61.15 ± 5.91	12.43 ± 2.38
PP-WF/DAP ₂₅	4142.6 ± 295.4	54.41 ± 4.12	11.83 ± 2.01
PP-WF/OP ₃₀	3936.4 ± 218.3	30.70 ± 1.98	5.29 ± 0.73

cantly decreases. This trend agrees well with the unnotched impact strength results. However, the addition of DAP slightly decreased the mechanical properties. This may be due to a good interaction of DAP and WF, indicating strong compatibility between them. In conclusion, DAP flame retardants can effectively improve the fire retardancy with almost no reduction in the mechanical properties of the PP-WF composites.

4. Conclusions

DAP and OP have been demonstrated to be effective flame retardant additives for WPC based on PP. The fire performance of flame-retardant PP-WF composites with these nonhalogen FRs is significantly improved. A loading of 25 wt% DAP results in a UL-94 V-0 rating, and 30 wt% OP loading provides a rating of UL-94 HB standard. The onset decomposition temperature and the weight loss of PP-WF/DAP are lower than those of PP-WF. This indicates that the addition of DAP increases the first-step decomposition of the PP-WF composite and promotes char formation. Meanwhile, the addition of OP increases the thermal stability of the PP-WF composite markedly in all temperature ranges, and the char layer reduces the combustion rate of the composite material. Then, the thermal behavior of PP-WF/OP shifts to higher temperatures than that of PP-WF. FTIR, SEM, and XPS analyses indicate that the dense, compact, and continuous char layers protect the PP-WF composite from the transfer of fire, flammable gases, and heat. There is an interaction between FR and/or the decomposition products of FR and PP-WF composite and/or the decomposition products of PP-WF that does not notably reduce the mechanical properties of flame-retardant WPC.

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