

RESEARCH ARTICLE

The utilization of phytic acid as a reactive flame retardant in the preparation of a fully waterborne biobased epoxy system

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Abstract

A fully biobased waterborne flame-retarded epoxy system was prepared using sorbitol polyglycidyl ether epoxy resin (SPE) and phytic acid (PA) as a reactive flame retardant (FR). The flame-retardant efficiency was evaluated by comparing the reference SPE-PA system with solventborne and waterborne SPE systems. Additional enhancement of intumescence and reduction of flammability was achieved by incorporating ammonium polyphosphate (APP) and melamine (MEL) into the SPE-PA system. PA, serving as a curing agent, contributed approximately 1% phosphorous content, resulting in an increased limiting oxygen index (LOI). UL-94 flammability tests demonstrated improved FR properties with PA, and the addition of 2% phosphorous from APP to SPE-PA achieved a self-extinguishing V0 UL-94 rating. Thermogravimetric analysis (TGA) revealed enhanced thermal stability and higher char yield with PA compared with other curing agents. Mass loss calorimetry (MLC) confirmed the superior charring effect of PA compared with other curing agents. The thermal insulation properties of the residual char were assessed by measuring the temperature on the back surface (T_b) of coated steel plates exposed to a 25 kW/m² heat flux for 1 h. The PA sample containing 3%P of APP exhibited a T_b decrease of 130°C compared with the solventborne reference sample. Scanning electron microscopy analysis of the char morphology supported these findings, indicating the effectiveness of the intumescent FR system. Infrared spectra of the char residues and pyrolysis gaseous products were obtained to gain insights into the flame-retardant mechanism of the different systems.

KEYWORDS

fully biobased epoxy, intumescent flame-retardant system, phytic acid, reactive flame retardant, self-extinguishing system, waterborne epoxy

1 | INTRODUCTION

Epoxy resins have been recently used in various industries like composites, coatings, transportation, and electronics.¹ However, maintaining their remarkable mechanical and thermal properties is a big challenge for academia and industry because of environmentally benign trends.² Many studies have been conducted on bioresources such as cellulose,

lignin, isosorbide, plant oils, amino acids, and itaconic acid to produce epoxy resins or curing agents.³ The waterborne epoxy systems are preferred compared with the solventborne systems from the green chemistry point of view.⁴ Accordingly, by using biobased flame retardants, a fully biobased flame-retardant epoxy system can be prepared.

Currently, flame retardants (FRs) are one of the main components almost in all polymeric materials to reduce fire hazards. They can be

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added to the polymer by direct physical blending, or chemically incorporated into the polymer structure. Intumescent FR coatings have been widely used to protect steel structures against fire,⁵ and recently it is reported they can be applied to protect polymer substrates.⁶ Epoxy resin was suggested as a polymer binder due to its good adhesion to many surfaces.⁷

Nitrogen-containing FRs decompose during combustion to produce nitrogen, ammonia, and other N-containing inert gases which can dilute the concentration of oxygen and flammable gases in the combustion zone, those gases also can help to expand the char and promote the barrier effect of intumescent FR systems.⁸ Melamine (MEL) and other N-containing FRs are usually used in combination with other FRs like phosphorus-containing compounds.⁹ These FRs are good candidates to replace harmful halogen-containing FRs due to their high efficiency.¹⁰ The phosphorus-containing groups can be presented as reactive FRs whether they are part of the epoxy monomer or the curing agent.¹¹ In particular, phosphate-containing compounds improved the flame-retardant efficiency due to the higher char formation activity compared with other phosphorous FRs.¹²

The intumescent system used in FR coatings mainly consists of three additives: an acid source that catalyses the dehydration reactions (e.g., ammonium polyphosphate, APP), a carbon source that acts as a char promoter (e.g., pentaerythritol), and blowing agent to release inert gases and present a porous char layer (e.g., melamine), the resulting barrier can decrease heat and mass transfer between the flaming zone and the underlying material.⁹

Phytic acid (PA), also known as inositol hexaphosphate, has attracted some attention to be used as a flame retardant due to the high P-content (28%).¹³ Under heat flux, PA acts as an acid source to promote char formation.¹⁴ It showed a self-extinguishable behavior when it was used with chitosan to form a coating deposited on cotton fabric.¹⁵ This mixture showed also a good fire-retardant performance via the formation of a highly stable char when it was incorporated into an ethylene-vinyl acetate (EVA) copolymer.¹⁶

Phytic acid has been applied mostly in flame retardance for fabrics since it can be used as a dopant.¹⁷ It has been used with sulfonated melamine-formaldehyde between chitosan layers in a layer-by-layer deposition method for cotton, which improved the char yield by 32% compared with uncoated cotton.¹⁸ PA has been used also in combination with silicon-containing compounds for cotton fabrics, as a result, to increase the thermal stability more thermally stable charred residues were observed.¹⁹

Phytic acid has been used as a cross-linking agent for epoxidized natural rubber (ENR) latex to form an elastomer with good mechanical and thermal stability; however, 40% of PA was needed to present the self-extinguishing UL-94 rating (VO).²⁰ Another method to utilize PA was applying it as a coating for PLA. Its activity was presented by increasing LOI and decreasing HRR significantly; however, it was more advantageous to use phytate salts to limit the migration of PA if it is incorporated alone into polylactic acid (PLA).²¹

The past research on biobased and waterborne FRs has made some progress; however, developing highly efficient biobased FRs for polymers remains a challenge. In previous work, the SPE solventborne

system was prepared by using a cycloaliphatic amine curing agent,²² and SPE fully waterborne system was prepared by using an alkylated polyalkylene polyamine curing agent.²³ The results obtained for SPE-SB-Ref and SPE-WB-Ref samples will be mentioned for the sake of comparison. Their measurements have been repeated together with the phytic acid samples and showed only minor deviations. This study aims to improve the flame-retardant properties of the sorbitol-based epoxy monomers further by using phytic acid as a reactive FR to prepare a fully waterborne biobased epoxy system.

2 | MATERIALS AND METHODS

2.1 | Materials

ERYSIS GE-61, a waterborne SPE epoxy monomer (epoxy equivalent mass: 160–195 g/mol, viscosity at 25°C: 4–7 Pa s), and a solventborne SPE epoxy monomer ERYIS GE-60 (epoxy equivalent mass: 160–190 g/mol, viscosity at 25°C: 7–9.5 Pa s) were supplied by Emerald Performance Materials (NJ, USA).

Phytic acid (50% solution in water), was bought from Sigma-Aldrich (Darmstadt, Germany), with a density of 1.432 g/mL at 25°C. An alkylated polyalkylene polyamine hardener Anquamine 401 (non-volatile content: 70%, amine hydrogen equivalent (AHEW): 200 g/eq, viscosity at 25°C: 30 Pa s) was provided by Evonik Industries (Essen, Germany). A cycloaliphatic amine hardener MH 3122 (amine hydrogen equivalent: 60 g/eq, viscosity at 25°C: 80–120 mPa s) was provided by IpoX Chemicals (Budapest, Hungary).

A fine-grained ammonium polyphosphate (phase II) Exolit AP422 (P-content: 31–32%) was acquired from Clariant International Ltd. Melamine (MEL) 99% was bought from Sigma-Aldrich (Darmstadt, Germany).

2.2 | Methods

2.2.1 | Samples preparation

The mixing ratio to produce the reference solventborne sample (SPE-SB-Ref) is 1:3 for cycloaliphatic amine hardener and SPE monomer.²² The mixing ratio to produce the reference waterborne sample (SPE-WB-Ref) is 1:2:2.7 for water, alkylated polyalkylene polyamine hardener, and SPE monomer.²³ The reference phytic acid sample (SPE-PA) was prepared according to the mixing ratios mentioned in Table 1. This sample contains around 1%P from phytic acid.

APP-containing samples were prepared to provide further 1, 2, and 3% of phosphorous content into the SEP-PA system, the amount of APP added to prepare those samples was 3.2, 6.4, and 9.6%, respectively, and the used abbreviations are APP1, APP2, and APP3. Melamine (MEL) samples were prepared by using 5% MEL according to preliminary tests. To investigate the cooperative effect of MEL with APP, a 5% MEL was used with the sample APP3. The components of each sample were mixed evenly and left for 7 days at room temperature to be cured in suitable silicone moulds under ambient conditions. The samples for mass loss

TABLE 1 The cured epoxy system components and their mixing ratios.

Material description	Content in the system (%)
Water-soluble SPE epoxy monomer ERY SIS GE-61	77
Phytic acid (50% solution in water)	7.7
Distilled Water	15.3

measurements were placed in aluminium sheets after curing without any adhesion. However, the samples for heat insulation measurements were prepared differently, after mixing the components, they were coated on steel plates and left 7 days at room temperature for curing.

2.2.2 | Characterization of fire behavior

The limiting oxygen index (LOI) indicates flame retardancy since it represents the minimum concentration of oxygen required to support the combustion within a controlled oxygen/nitrogen mixture of a sample burned in a candle-like setup according to the standard ASTM D-2863. The sample dimensions for LOI and UL-94 are 120 mm × 15 mm × 4 mm.

The UL-94 tests of the samples were carried out by applying a bunsen burner fire horizontally and vertically on the free end of the sample according to the standards ISO 9772 and ISO 9773, respectively.

The combustion properties and potential fire hazard were evaluated by a mass loss type cone calorimeter (MLC) produced by FTT Inc. The measurements have been done according to ISO 13927 under a heat flux of 25 kW/m² and an ignitor to initiate the combustion. The thermopile method was employed. The dimensions of the samples were 100 mm × 100 mm × 2 mm. The heat release rate (HRR) was measured on a time scale where the time to ignition (TTI) and extinguishing can be defined. The peak heat release rate (pHRR), the time to reach this peak, and the total heat release (THR) were measured to compare the combustion properties for the reference and flame-retardant samples. The reference sample was measured three times, with deviations within the acceptable error range ($\pm 10\%$ ²⁴), and the FR samples were measured once.

2.2.3 | Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were conducted using a TA Q5000 device at a heating rate of 10°C/min in the range of 25–600°C under 25 mL/min flow rate of N₂ gas. The mass of each sample was around 5 mg, and the sample pans were Platinum-HT type.

2.2.4 | Heat insulation efficiency measurements

The formulations were coated at 1 mm thickness onto steel plates of dimensions 100 mm × 100 mm × 1 mm. Two thermocouples were

used to obtain the average temperature on the back side of the steel plates for 1 h in the mass loss calorimeter under a heat flux of 25 kW/m².

Type K Thermocouples were used. The thermocouple cable was firmly secured by a clamp on a stand adjacent to the cone calorimeter. The sensing parts of the thermocouples were inserted into the sample holder through a dedicated hole on the side of the sample holder. This placement ensured that the thermocouples were positioned between two aluminum sheets, each 0.2 mm thick, and beneath the coated steel plate coated with the coating samples. Subsequently, a 0.5-mm-thick steel plate was placed, followed by glass wool, which served as the bottom layer in the sample holder. This arrangement provided the necessary insulation and support for the experimental setup.

2.2.5 | Attenuated total reflection infrared (ATR-IR) analysis

The compositional analysis of the residual char after MLC tests was carried out by using a Bruker Tensor 37 FTIR spectrometer equipped with a SpecAc GoldenGate ATR. The wave number region is 4000–600 cm⁻¹, and the resolution is 4 cm⁻¹. Small portions from both the top and underlying parts of the char were mixed and then pressed against the diamond of the ATR apparatus.

2.2.6 | Scanning electron microscopy (SEM)

The charred residues after MLC were coated with a thin golden layer and analyzed by a scanning electron microscope JEOL JSM-5500 (JEOL Ltd., Japan) at 15 keV accelerating voltage to investigate the microstructure of the char.

2.2.7 | Laser pyrolysis–Fourier transform infrared (LP-FTIR) analysis

The chemical characterization of the degradation gases of the samples was carried out by using a Bruker Tensor 37 FTIR spectrometer coupled with carbon dioxide laser equipment (SYNRAD 48-1, USA). The pyrolytic degradation gases can be analyzed instantaneously.²⁵

3 | RESULTS AND DISCUSSION

3.1 | Limiting oxygen index (LOI) and UL-94 flammability tests results

The tested sample's combustibility can be indicated by comparing their limiting Oxygen index (LOI) values. UL-94 flammability tests in vertical and horizontal positions are used to classify the different samples into different categories based on their flammability. The results are summarized in Table 2.

TABLE 2 LOI values and UL-94 ratings for SPE reference, APP, and MEL samples.

Sample name	LOI (%)	UL-94 rating
SPE-SB-Ref	22	HB (20 mm/min)
SPE-WB-Ref	22	HB (22.7 mm/min)
SPE-PA-Ref	24	HB (vertical test; burning up to the clamp)
APP1	30	HB (vertical test; burning up to the clamp)
APP2	39	V0
APP3	55	V0
MEL (5%)	31	V1 (vertical test; Burning time: 15 s)
MEL (5%) + APP3	53	V0

SPE-SB-Ref and SPE-WB-Ref samples showed 22% LOI values indicating that these reference systems are easily flammable,^{22,23} while SPE cured with phytic acid, increased LOI to 24% due to the phosphate groups in the PA structure that can present flame-retardant activity.²⁶ UL-94 measurements also showed that SPE-SB-Ref and SPE-WB-Ref samples present higher flammability since they failed in the horizontal burning test, while the SPE-PA-Ref sample passed the horizontal burning test, but still shows an HB rating since it failed in the vertical burning test.

The addition of APP to the SPE-PA system increased LOI even further due to the activity of the extra phosphate groups provided by APP in the formation of a char layer which suppresses oxygen permeation and inhibits the volatile degradation products from escaping to the combustion zone. LOI was significantly high in the case of the APP3 sample (55%) which is due to the formation of a thick, insulating char that also permits the self-extinguishing UL-94 rating V0 at 2%P content from APP. Later, among APP samples, only the results of the APP3 sample will be discussed.

When 5% melamine was used in the SPE-PA system, the LOI value increased to 31%, which is sufficient in terms of flame retardancy.²⁷ This value is like the LOI of the APP1 sample; however, the UL-94 rating in the case of MEL was better than that in the case of the APP1 sample. The latter failed in the vertical burning test, like the SPE-PA-Ref system, while the addition of 5% MEL permitted a V1 rating with 15-s burning time, which is very close to reaching the self-extinguishing V0 rating. This can be explained by nitrogen volatiles and ammonia gases released by melamine decomposition that can act as diluents reducing the concentration of flammable gases in the flaming zone, besides its contribution to the charring effect.⁷ The sample MEL(5%) + APP3 showed relatively the same results as the APP3 sample, which is extremely good.

3.2 | Thermogravimetric analysis (TGA)

Various parameters, like the onset temperature of degradation (T_{onset}), the temperature of losing 50% of the sample mass (T_{-50}), the

maximum mass loss rate (dTG_{max}), the temperature at this point, and the char yield at 600°C are also summarized in Table 3. For temperature measurements, the uncertainty is approximately $\pm 1.5^\circ\text{C}$, and for mass measurements, it is approximately $\pm 2\%$ based on our previous experiences with the instrument used. The onset temperature is defined according to the standard ISO 11358-1 as the point at which the baseline representing the starting mass “after evaporation” intersects with the tangent line drawn to the TGA curve at the location of the maximum gradient.

The evaporation of water from the waterborne systems (i.e., all systems excluding SPE-SB-Ref sample) is the first reaction presented in Figure 1 by a mass loss step around 100°C with a 3%–10% mass decrease. The thermal degradation behavior of SPE cured with phytic acid is different compared with SPE-SB-Ref and SPE-WB-Ref systems. The thermal decomposition of the SPE-PA-Ref system starts at lower temperatures due to the catalytic effect of phosphoric acid produced by the degradation of phytic acid.²⁸ The other remarkable change is that SPE-SB-Ref and SPE-WB-Ref systems showed two steps of degradation. SPE-SB-Ref and SPE-WB-Ref systems lose approximately 50% of their masses during the first step up to around 330 and 340°C , respectively. The mass loss in this range might be explained by the degradation of the epoxy matrix started with dehydration and elimination reactions on epoxy chains, which will be subject to chain scission and fragmentation reactions till the formation of carbonaceous char. At higher temperatures, this char will be decomposed in different mass loss rates as observed in the SPE-SB-Ref and SPE-WB-Ref TGA curves in Figure 1. SPE-PA-Ref system showed only one step of degradation, which can be attributed to the enhanced thermal stability due to cross-linking SPE chains with phytic acid rings comparing with the SPE-SB-Ref and SPE-WB-Ref cured with cycloaliphatic amine and polyalkylene polyamine, respectively.

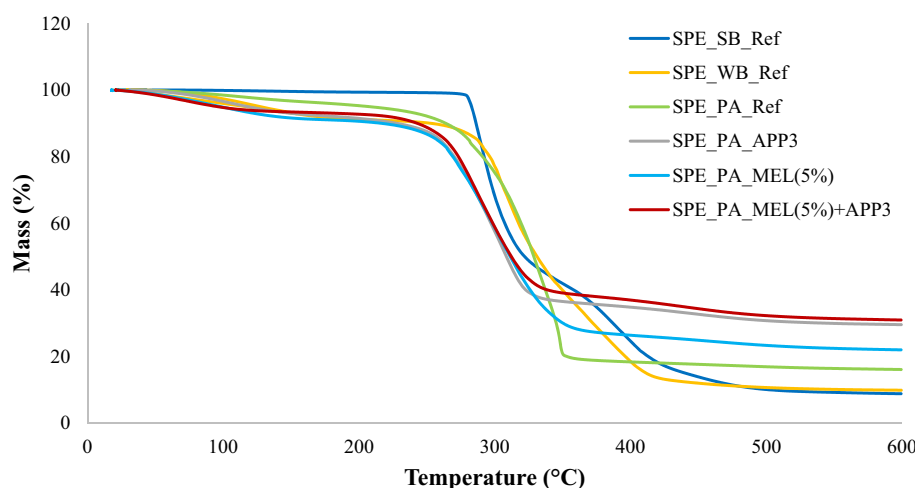
At around 350°C , the SPE-PA-Ref sample showed only a minor mass loss till 600°C due to the higher char yield (almost twice the weight compared with SPE-SB-Ref and SPE-WB-Ref samples) and the higher thermal stability of the formed char, which proves of the charring effect of phytic acid. Furthermore, it has been stated that the higher char yields of thermosets in a nitrogen atmosphere indicate better flame retardancy.²⁹

It can be seen from Table 3 that APP has nearly no impact on the T_{onset} values since the thermal degradation of the APP itself starts at around 290°C . The weight loss of the samples showed a dramatic change at higher temperatures (320 – 340°C), which is around the temperature of the maximum degradation peak for APP.⁷ As a result, the formed polyphosphoric acid can initiate the char formation and intumescence which can slow down the weight loss in the matrix and increase the char yield.²⁶

The maximum dTG values shown in Table 3 reveal that increasing P content from 1% of the reference SPE-PA sample to 4% in APP3 sample decreased the maximum weight loss rate. This can be explained by the more intense char-forming activity of APP at the beginning of the degradation compared with that of phytic acid alone. As the matrix is carbonized, less volatiles have been released, thus decreasing the degradation rate.

TABLE 3 TGA results for SPE reference, APP, and MEL samples.

Sample name	T _{onset} (°C)	T ₋₅₀ (°C)	dTG _{max} (%/°C)	T _{dTGmax} (°C)	Char yield at 600°C (%)
SPE-SB-Ref	288.8	322	1.72	290	8.9
SPE-WB-Ref	287.2	331.2	1.13	302.1	9.9
SPE-PA-Ref	287.0	331.6	2.62	348.1	19.7
APP3	263.7	317.5	0.95	298.0	36.9
MEL (5%)	260.7	323.6	0.83	295.0	30.6
MEL (5%) + APP3	254.7	324.4	0.88	298.5	37.6

**FIGURE 1** TGA curves of SPE reference, APP, and MEL samples.

When 5% melamine was added to the SPE-PA-Ref system, the onset temperature of degradation did not change significantly. Since melamine starts decomposing at around 280°C and gets 100% weight loss around 370°C to release NH₃ gas, which can blow the charring layer by forming micropores and improve the intumescence initiated by the phosphate group in phytic acid,⁷ the lowest degradation rates were measured in MEL-containing samples. The char yield was 30.6%, in the case of the SPE-PA-MEL(5%) sample (increased by 11% compared to the SPE-PA-Ref sample), indicating the contribution of melamine to the charring effect by reacting with phosphorus acid groups from phytic acid to form a melaminium salt structure, primarily melamine phosphates and polyphosphates. These compounds exhibit relatively high thermal stability.³⁰

When MEL was applied together with APP, it provided the system with more phosphate groups and was also a source of blowing agent. The char yield of the MEL(5%) + APP3 sample is 37.6%, which is almost twice the char amount compared with the SPE-PA-Ref sample, but it is only 1% higher than the char yield of the APP3 sample.

3.3 | Mass loss calorimetry results

To investigate the combustion properties and potential fire hazard of the different SPE systems, some key parameters were measured, like time to ignition (TTI) as the ignition initiated with a spark ignitor. By measuring the released heat after combustion, the peak heat release

rate (pHRR) and the total heat release (THR) can be calculated, which are very important parameters for fire safety evaluation and understanding the fire behavior of materials.³¹ The shift pHRR in time can be presented by comparing fire growth rate values (FIGRA = pHRR/t_{pHRR}). The cone calorimetry results are summarized in Table 4.

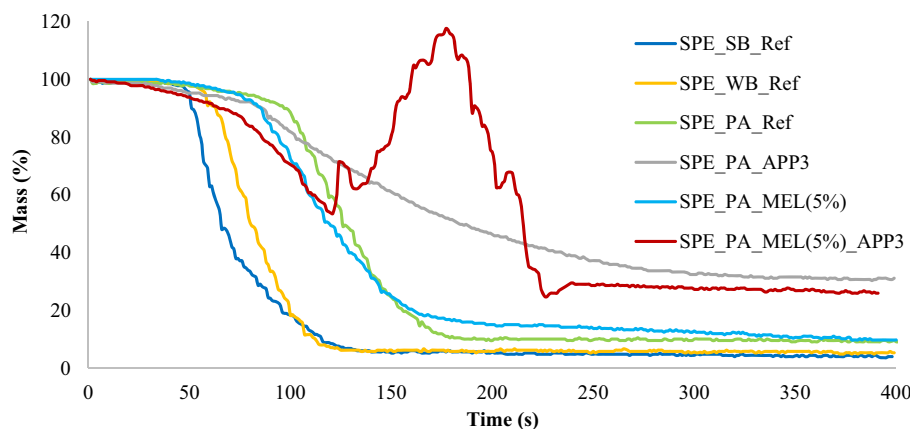
The activity of PA as a reactive flame retardant in the sorbitol polyglycidyl ether epoxy system can be indicated also by increasing the time to ignition value compared with SPE-SB-Ref and SPE-WB-Ref systems which showed 53 and 58 s, respectively.^{22,23} The released water can dilute the combustible gases produced by the decomposition of the sample surface and as a result, postpone the ignition. Furthermore, it was noticed during the measurements that the char layer was formed even before the ignition because of the dehydration effect of PA. Through this reaction, pyrophosphate or polyphosphate might be formed to promote the formation of a char layer, that is, carbonizing the epoxy matrix. According to Table 4, the SPE-SB-Ref sample needs 30 s to reach the time of pHRR starting from between TTI, indicating that this system undergoes a relatively quick-growing fire. This duration increased in the case of the SPE-WB-Ref system to 39 s and reached 50 s in the case of SPE-PA-Ref, indicating that phytic acid not only delayed the ignition of the epoxy matrix but also increased the time to the peak of heat release rate (HRR), potentially resulting in a slower buildup of fire intensity.

Mass loss curves for the cone calorimetry results are shown in Figure 2 to offer a more comprehensive view of the data. The main mass loss steps for all samples are around their time-to-ignition values. The

TABLE 4 Cone calorimetry results for SPE reference, APP, and MEL samples.

FR composition	TTI (s)	pHRR (kW/m ²)	t _{pHRR} (s)	THR (MJ/m ²)	Residue (%)	FIGRA (kW/m ² s)
SPE-SB-Ref	53	498.9	83	58.5	6.4	6.0
SPE-WB-Ref	58	412	97	33.4	4.2	4.25
SPE-PA-Ref	96	287.8	146	25.2	9.4	1.97
APP3	100	104.7	172	15.4	31.4	0.61
MEL (5%)	90	211.6	142	20.5	8.3	1.49
MEL (5%) + APP3	93	95.9	130	11.2	28.5	0.74

Abbreviations: FIGRA, fire growth rate; PHRR, the peak of heat release rate; t_{pHRR}, the time of the peak of heat release rate; THR, the total heat released; TTI, time to ignition.

FIGURE 2 Mass loss curves of SPE reference, APP, and MEL samples.

mass is gradually decreased in the case of APP samples; however, the peak noted in the case of MEL(5%) + APP3 sample is due to the extreme intumescent effect that can produce intumescent char reaching the cone of the instrument and putting extra pressure on the scale, which may have influenced the incorrect mass loss results.

In the case of the SPE-PA-Ref sample, pHRR values compared with SPE-SB-Ref and SPE-WB-Ref systems decreased by 42% and 30%, respectively, and THR values decreased by 57% and 25%, respectively.^{22,23} The residual char mass of the SPE-PA-Ref sample was 9.4%, which is significantly higher compared with the char yield of SPE-SB-Ref (6.4%),²² and SPE-WB-Ref (2.2%),²³ as the PA led to the formation of a thermally stable char which remain stable as one piece after the flame extinguishing as can be seen in Figure 3C, while the char was fragmented and residues accumulated along the edges of the aluminum plates in the case of SPE-SB-Ref and SPE-WB-Ref samples as shown in Figure 3A, B. This phenomenon can be attributed to the lower char yield and reduced thermal stability exhibited by these samples. Therefore, this observation aligns well with the findings from the TGA analysis.

The results in Table 4 showed that THR decreased by increasing P content, THR was decreased by 39% (from 25.2 to 15.4 MJ/m²) in the case of the APP3 sample. Due to the chemical modification of the degradation of the polymer (i.e., more charring, and accordingly less release of combustible gases), the THR was significantly reduced, and the amount of char residue increased since the formed char layer can retard the escape of volatile degradation products from the combustion zone and

suppress oxygen permeation. The char photos (shown in Figure 3) support this conclusion as they show a thicker char that can act as a heat shield to decrease the heat release rate and elongate the time of heat release consequently resulting in lower FIGRA values.

Fire growth rate curves are shown in Figure 4.

When comparing FIGRA curves with HRR curves, it becomes evident that these curves exhibit similar behaviours for corresponding samples. However, a more pronounced gap is observed between the FIGRA curves of SPE-PA samples and SPE-SB-Ref and SPE-WB-Ref samples. Notably, the SPE-PA-MEL(5%) and SPE-PA-APP3 samples demonstrate higher FIGRA values compared with the SPE-SB-Ref and SPE-WB-Ref samples after the FIGRA peaks of the SPE-SB-Ref and SPE-WB-Ref samples. Such a pattern suggests that the SPE-PA-MEL (5%) and SPE-PA-APP3 samples may exhibit slower fire growth, a desirable characteristic in flame-retardant systems.

Figure 5 plots the HRR and THR curves of the tested samples, respectively. The pHRR decreased by 64% (from 287.8 to 104.7 kW/m²) in the case of the APP3 sample due to the activity of APP in promoting the formation of intumescent char over the flaming zone that can slow down the thermal degradation of the matrix and retard the heat release.

It can be seen in Figure 5 that the samples containing melamine started to release heat earlier compared with SPE-PA-Ref and APP3 samples since the degradation of MEL starts at somewhat lower temperatures.⁷ For the same reasons, FIGRA values were lower. However, the 5%MEL sample showed lower HRR compared with the

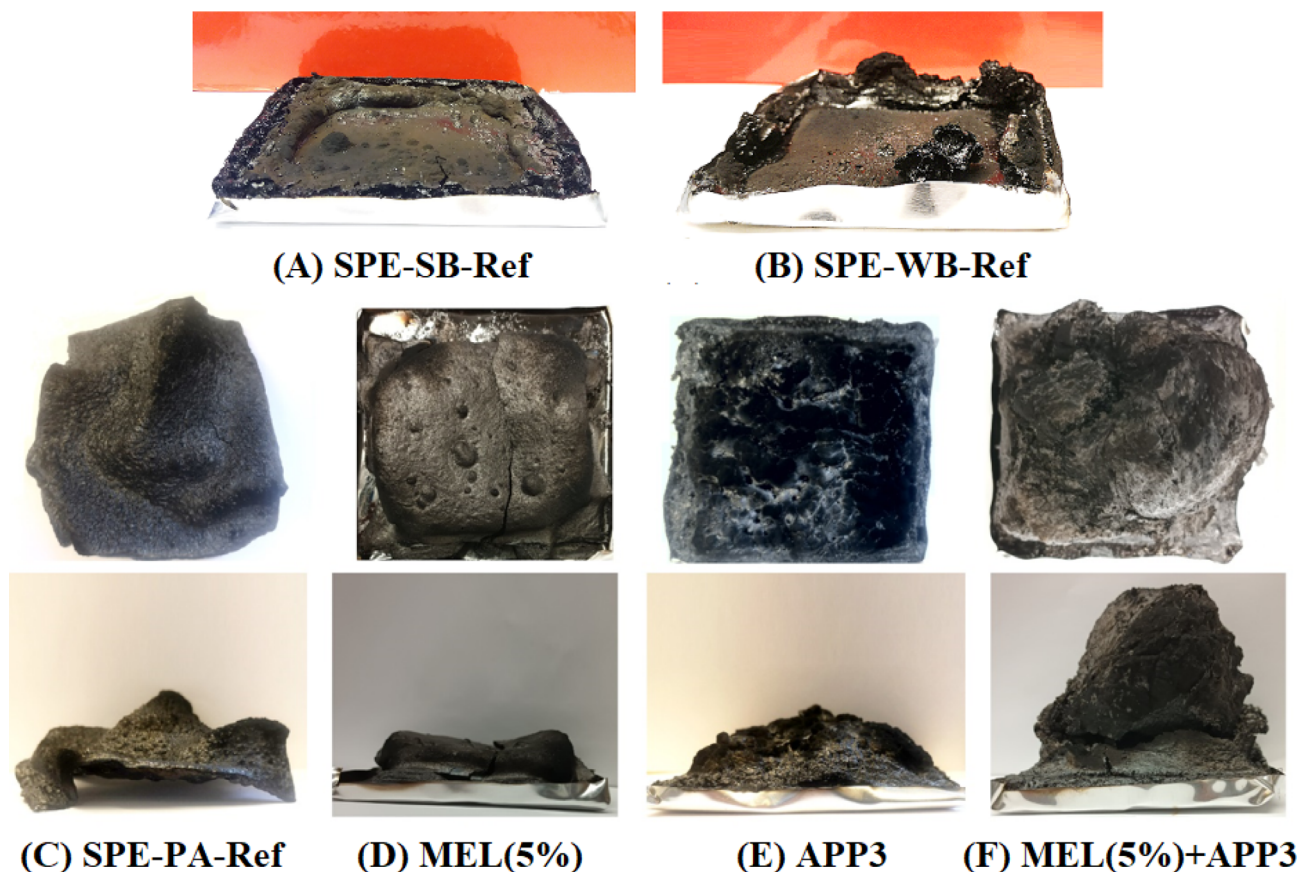


FIGURE 3 Photos of the MLC char residues for SPE reference, APP, and MEL samples.

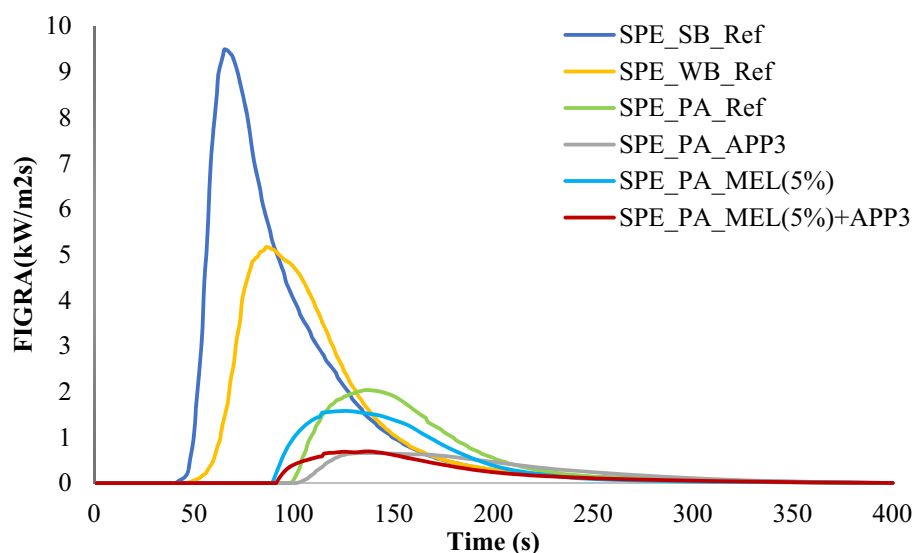


FIGURE 4 Fire growth rate (FIGRA) curves of SPE reference, APP, and MEL samples.

SPE-PA-Ref sample (pHRR decreased by 26.5% and THR decreased by 18.7%) due to its activity as a blowing agent of the formed char that enhances the barrier effect to decrease heat and mass transfer between the flaming zone and the underlying material.⁹

When MEL was used alone or with APP, it prepones the TTI and the time of pHRR, but it decreases the heat release from the burning samples. In the case of the MEL(5%) + APP3 sample, pHRR decreased

by 8.4% and THR decreased by 27.3% compared with the APP3 sample. The more pronounced impact on the THR might be explained by the improved intumescent effect presented by melamine since the intumescent layer becomes less compact but spongier, in conclusion, the heat insulation effect is improved since more mini pores were formed and acted to protect the inner material, this can be well observed later in SEM micrographs.

FIGURE 5 Heat release rate (HRR) and total heat release (THR) curves of SPE reference, APP, and MEL samples.

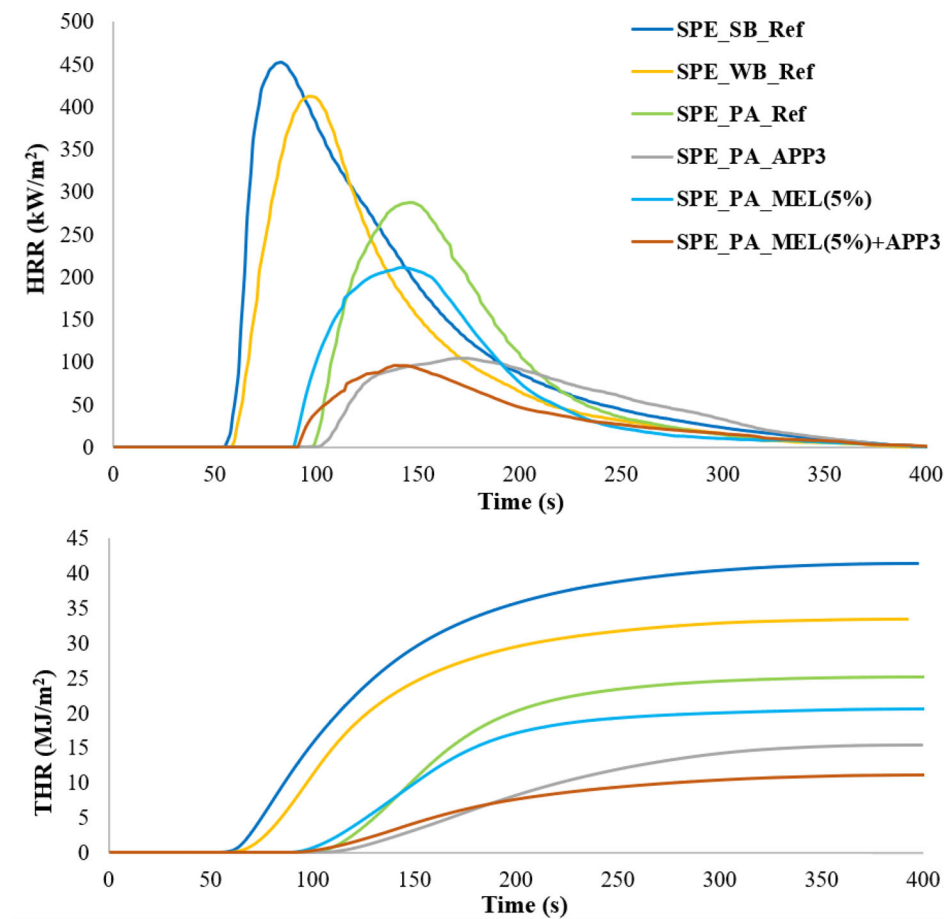
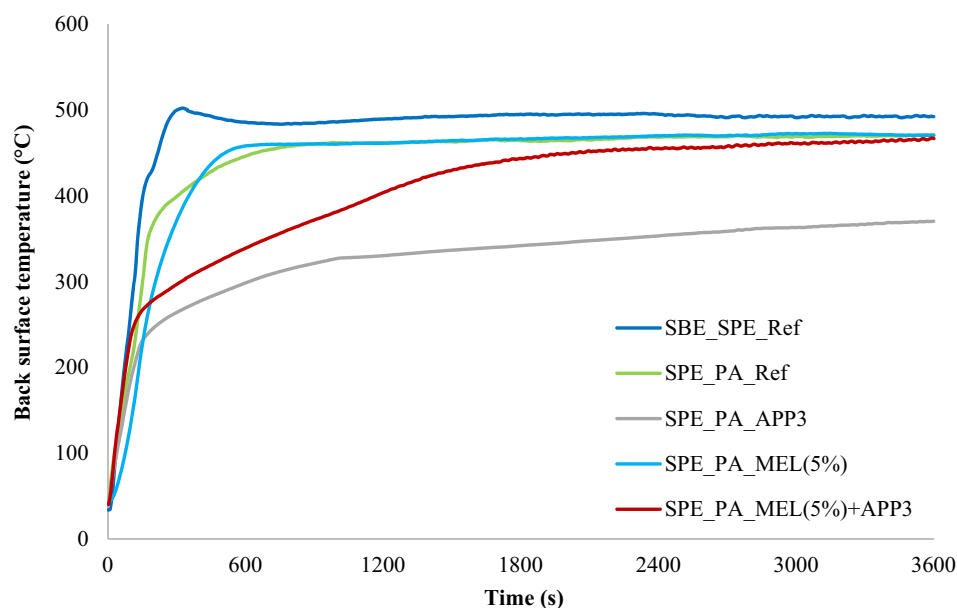


FIGURE 6 Comparison of back surface temperatures of SPE reference, APP, and MEL samples.



3.4 | Back surface temperature results

To investigate more deeply the heat insulation potential of the prepared fully biobased epoxy systems, they were applied as 1 mm-thick coating on 1 mm-thick steel plates. The back surface temperatures

(T_b) of the coated steel plates were plotted as a function of time during 1 hour of heat exposure (25 kW/m²) in Figure 6.

The critical temperature for deteriorating the steel properties is around 500°C.³² Since the thermocouples are on the back surface behind a piece of aluminum sheet and for safety reasons, the

considered failure temperature (T_f) is 400°C, and the required time to reach this temperature (t_{Tf}) is mentioned in Table 5. The uncertainty of the measured temperatures is approximately $\pm 10^\circ\text{C}$. The back surface temperature was not measured for the SPE-WB-Ref sample, since the 1-mm-thick coating showed many cracks after curing.

The maximum T_{b3600s} among the measured values was 493°C presented in the case of the SPE-SB-Ref sample; this sample also allowed the failure temperature of the back side after 152 s, which is relatively short. SPE-PA-Ref also allowed the failure temperature, but it took 302 s, which is more favorable during the early stages of a fire.

To enhance the insulation of the char, APP and MEL samples were prepared and tested. APP3 sample showed a 108°C reduction in the maximum temperature at the back surface suggesting more efficient thermal insulation properties for the formed char. It can be also observed in the char photos (Figure 7E) that APP permits the formation of continuous and compact char that present good thermal stability after heat exposure for 3600 s.

It can be observed in Figure 6 that the difference in back-side temperatures between SPE-PA-Ref and other samples (dT_b) is relatively small, particularly during the early stages of the test. However, as the tests progress, the difference in backside temperature becomes more significant in the case of samples containing APP due to the formation of intumescent char. On the measurement timeline, this happened after around 150 s, which is close to the time of peak heat release rates (pHRRs) as shown in the mass loss measurements (Figure 5). Notably, the char from the SPE-PA-MEL sample exhibited lower heat insulation performance compared with APP-containing samples. This char from the 5% MEL sample deteriorates early, resulting in lower heat insulation compared with the SPE-PA-Ref sample after approximately 390 s.

It can be observed in the photos in Figure 7B, C that both SPE-PA-Ref and SPE-PA-MEL samples present fragmented char after 3600 s, which can explain the lower thermal stability of the char. The melamine does not improve the heat insulation for a long time since its degradation starts at lower temperatures leading to the formation of gas channels within the formed char structure, which can be weak points for char breakdown. This effect can be seen also in the case of the SPE-PA-MEL(5%) + APP3 sample. Although the formed char of SPE-PA-MEL(5%) + APP3 sample in MLC measurements was thicker than other samples and permitted the lowest HRR and THR, it had a light and crumbly structure because of the swelling effect

improved by melamine, and as a result, the char lost its cohesion and adherence on the plate as shown in Figure 7E.

Thermocouples were placed at almost the same position; however, the char in the case of the MEL (5%) + APP3 sample peeled off during testing at different positions of the steel plate. This variability likely impacts the accuracy of temperature measurements. However, among the repeated measurements for the MEL (5%) + APP3 sample, all samples reached the failure temperature at different times.

3.5 | Attenuated total reflection-infrared spectrometry (ATR-IR) analysis of MLC residual char

To investigate the effect of the different flame-retardant compositions in the solid phase, the char residues received after mass loss calorimeter tests were subjected to infrared analysis. The recorded IR spectra in Figure 8 reveal that absorbance peaks corresponding to char residues from the SPE-PA-Ref sample include 1700 cm^{-1} ($\text{C}=\text{O}$), 1560 cm^{-1} (aromatic $\text{C}=\text{C}$), peak in the range ($1200\text{--}1050\text{ cm}^{-1}$) corresponding to $\text{C}-\text{O}-\text{C}$, all of which are the usual peaks in the IR spectrum of reference epoxy char.³³ These peaks can be seen also in SPE-SB-Ref and SPE-WB-Ref samples. However, some peaks representative of P-species like the peak in the region of $1050\text{--}855\text{ cm}^{-1}$ ($\text{P}-\text{O}-\text{C}$) shown only in the phytic acid reference sample which proves the activity of PA in promoting the formation of carbonaceous char rich in P-species.³⁴ The peak at around 1170 cm^{-1} ($\text{P}=\text{O}$) and the peak around 965 cm^{-1} representatives for the $\text{P}-\text{O}-\text{P}$ group can indicate the formation of ultra-phosphates because of dehydration reactions within the epoxy matrix initiated by the phosphate groups.³⁵

Similar peaks corresponding to $\text{P}=\text{O}$, $\text{P}-\text{O}-\text{P}$, and $\text{P}-\text{O}-\text{C}$ were observed in the case of the APP3 spectrum indicating that PA and APP present similar modes of action through the condensed phase. However, in the APP3 spectrum, higher peaks representative of $\text{P}-\text{O}-\text{C}$ were observed as a result of the increased $\text{P}-\text{OH}$ groups released by the thermal degradation of APP, which goes through esterification reactions with OH groups of the cured epoxy matrix.³⁵

$\text{P}-\text{O}-\text{P}$ peak showed higher intensity, but the peaks representative of aromatic $\text{C}=\text{C}$ and $\text{C}=\text{O}$ showed lower intensity, which might indicate the activity of APP in promoting the formation of more P-rich char, and less aromatization.

The addition of melamine did not present new peaks in the IR spectrum of the char since the melamine gaseous degradation products are released at the early stage of burning to act as flame inhibitors, as a result, the melamine sample showed quite similar peaks to SPE-PA-Ref sample.

3.6 | Scanning electron microscopy (SEM)

The char morphology can help to understand the solid-phase effect of flame retardants.³⁶ The micrographs of the cone calorimeter samples are shown in Figure 9.

TABLE 5 Back surface temperature results of SPE reference, APP, and MEL samples.

FR composition	T_{b3600s} ($^\circ\text{C}$)	t_{Tf} (s)
SPE-SB-Ref	493	152
SPE-PA-Ref	471	302
APP3	371	-
MEL (5%)	471	351
MEL (5%) + APP3	467	1166

Note: T_{b3600s} , back surface temperature after 3600 s, t_{Tf} , the time of reaching the failure temperature (T_f).

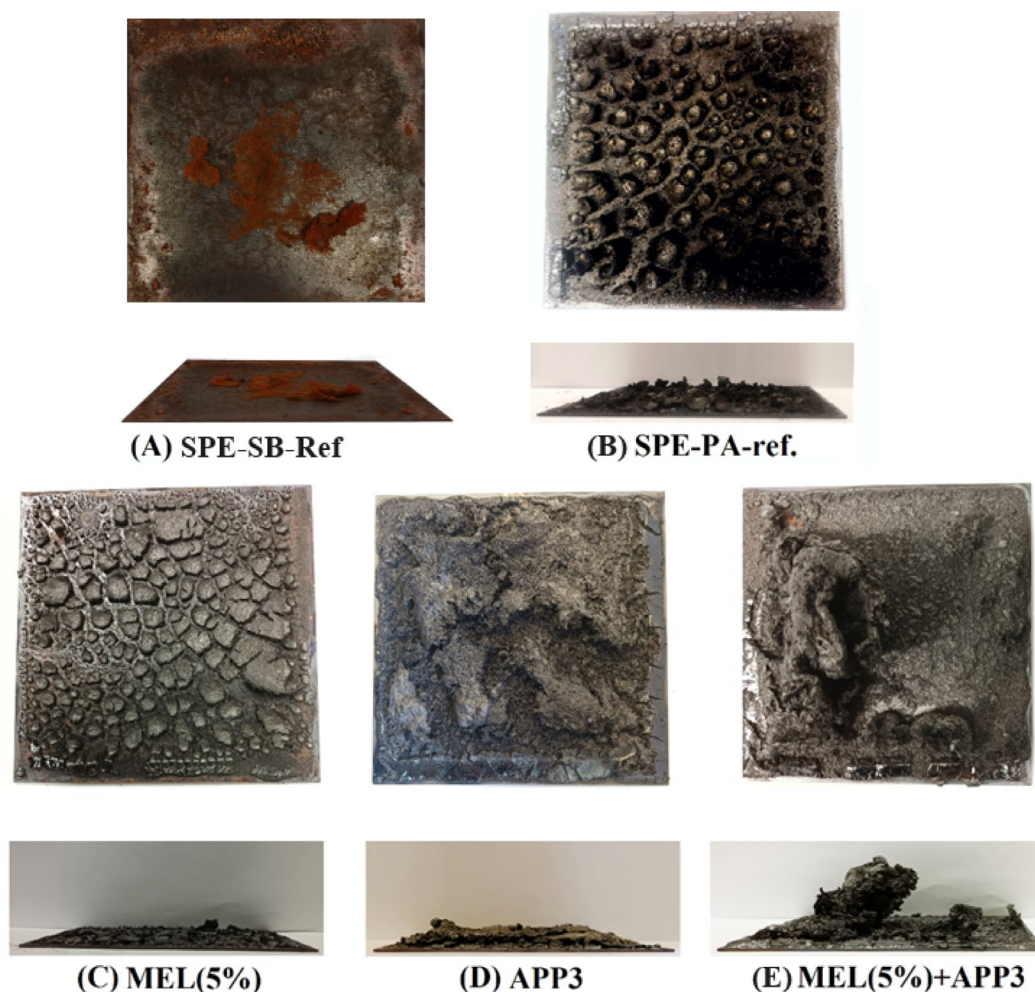


FIGURE 7 Photos of the char residues of the coated steel plates after MLC measurements for 3600 s.

Many micro-holes and cracks were observed in SEM micrographs of the residues of the SPE-SB-Ref sample after mass loss calorimetry.²² SPE-WB-Ref showed a less porous structure.²³ However, these structures have negligible influence on flame retardancy taking into consideration that the char has low thermal stability and becomes noncontinuous during burning, leaving most of the underlying surface uncovered as shown in MLC char photos in Figure 3. However, the SPE-PA-Ref sample presents continuous char after the measurement ends, and this char microstructure shows some micropores (Figure 9A); some pores and cracks also can be seen in the case of the 5% melamine sample (Figure 9B), which deteriorate the shielding effect of the char and increase the possibility of heat and mass transfer between the combustion zone and the underlying material, or the underlying substrate in case of coatings.

The char has a continuous and smooth surface in the case of the APP3 sample, the expansion can be observed at this microscopic level (Figure 9E), which is typical for intumescent flame-retardant systems. It can be stated that APP can initiate the intumescence of the char since the polyphosphoric acid produced by its decomposition can react with the OH groups of the epoxy matrix and lead to a series of dehydration and cross-linking reactions, as a result, multicellular layers

will be formed³⁷ that can act as an effective thermal barrier that can protect the underlying substrate against fire or heat transfer⁷ and can be seen even at the microscopic level of the sample containing MEL(5%) and APP3 (Figure 9D).

3.7 | Gaseous phase analysis by coupled laser pyrolysis-FTIR

The activity of PA, MEL, and APP in the gas phase was investigated by the analysis of thermal degradation products in the gas phase by laser pyrolysis coupled with FTIR.²⁵

IR spectra in Figure 10 reveal that absorbance peaks corresponding to decomposition products released in the gas phase for the SPE-PA-Ref include peaks located in the regions 4000–3000 cm^{-1} (O–H), in the region 3100–2800 cm^{-1} (aliphatic hydrocarbons C–H), especially methane at 3015 cm^{-1} , and in the region 1490–1300 cm^{-1} (H–C–H in methyl and methylene) which are released because of chain scission reactions of the cured epoxy matrix.³⁵ The peaks representative for aliphatic hydrocarbons in the case of SPE-PA-Ref showed considerably lower absorbance peaks compared with SPE-

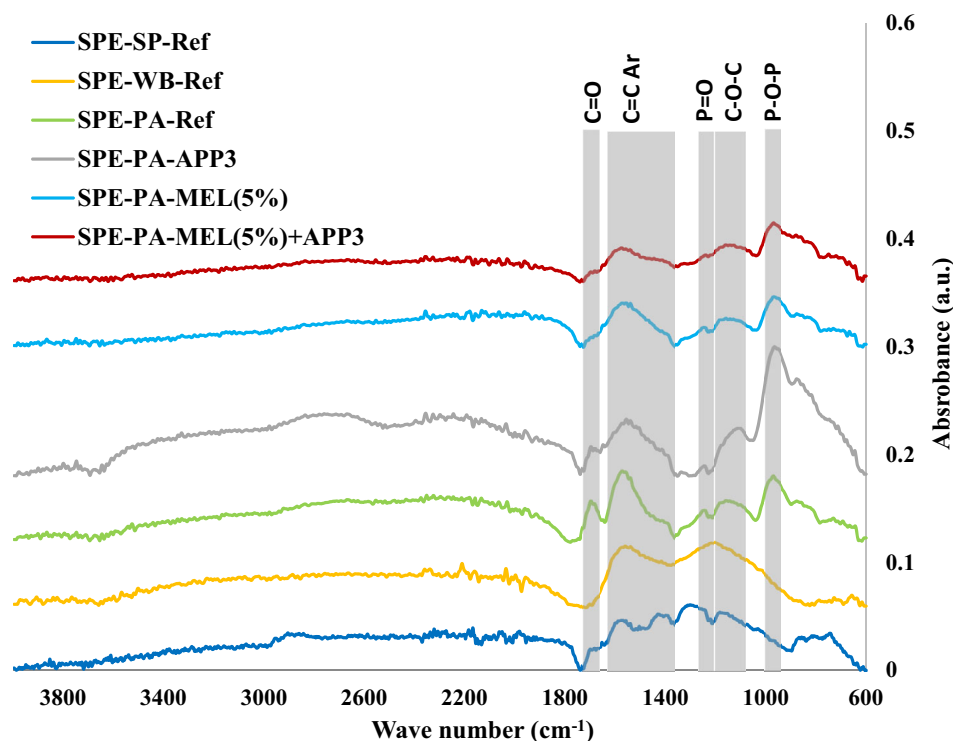


FIGURE 8 ATR-IR spectra of the MLC char residues of SPE reference, APP, and MEL samples.

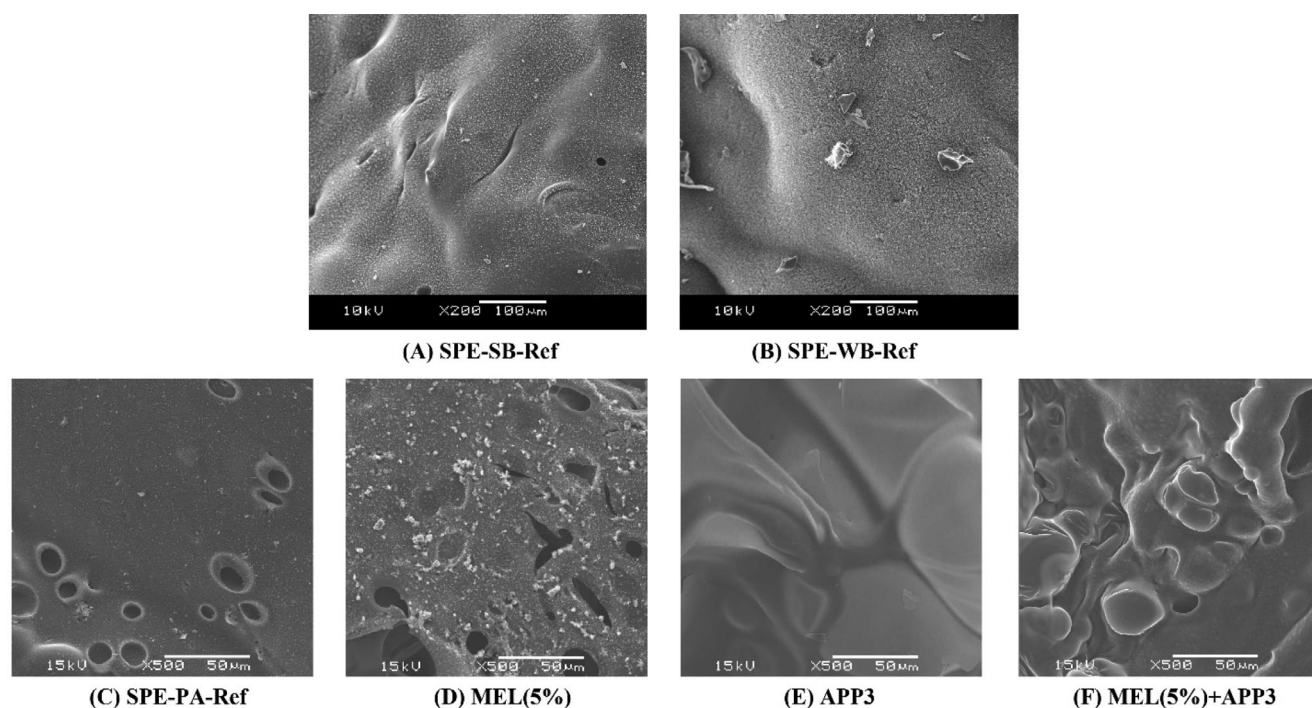


FIGURE 9 SEM images of the MLC char at $\times 500$ magnification for SPE reference, APP, and MEL samples.

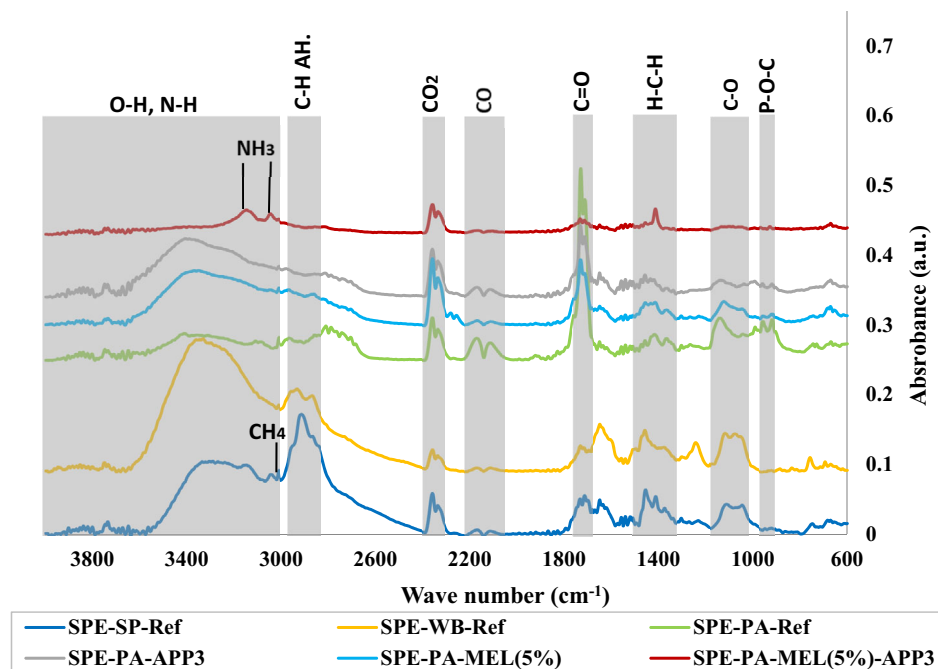
SB-Ref and SPE-WB-Ref samples indicating better thermal stability of the epoxy system.

However, SPE-SB-Ref and SPE-WB-Ref samples show similar peaks to SPE-PA-Ref, except for the P—O—C peak which appears due to phytic acid degradation. Another difference is that SPE-SB-Ref and SPE-WB-Ref samples showed higher peaks in the region 4000–

3000 cm^{-1} representative of N—H groups in the epoxy system cured with the alkylated polyalkylene polyamine hardener.

SPE-PA-Ref spectrum showed the highest intensities compared with other SPE-PA samples regarding the peaks in the region 1200–1000 cm^{-1} (C—O) and the peaks representatives of carbon monoxide (CO) in the region 2080–2200 cm^{-1} and that of carbon dioxide (CO_2)

FIGURE 10 LP-FTIR spectra of the gaseous degradation products of SPE reference, APP, and MEL samples.



in the region $2400\text{--}2300\text{ cm}^{-1}$. When adding either MEL or APP, the intensity of the formed CO decreased; however, the intensity of the peaks in the region $2400\text{--}2300\text{ cm}^{-1}$ representative of CO_2 exhibited mostly an opposite trend since CO_2 is the fractioning product of C—C and C—O bonds.³⁸ The sharp peaks around 1715 and 1730 cm^{-1} representative of the (C=O) group might indicate the formation of ketones or aldehydes as oxidation products of alcohols which are released by the decomposition of the cured SPE resin.

The presence of P-species was obvious in the solid phase as shown by the ATR results, as expected; however, some P-species can also be found in the gas phase as indicated by the presence of the signals at 920 and 960 cm^{-1} (P—O—C). The intensities of these peaks are the highest in the case of the reference SPE matrix cross-linked with phytic acid. Accordingly, PA might have some gas-phase radical-trapping effects as well, besides the significant charring in the condensed phase. When APP was used, the relative intensity of the peaks decreased, and the lowest intensities were observed when melamine was added with APP, which indicates the barrier effect of the formed char that improved by the additional phosphate groups presented by APP, and the increased condensed phase activity due to melamine addition, the char can suppress the escape of volatile degradation products.

It can be seen in Figure 10 that melamine and APP samples showed wide peaks in the region $3400\text{--}3000\text{ cm}^{-1}$ with higher intensity compared with the SPE-PA-Ref sample due to the presence of N—H besides O—H as a result of ammonia released from APP and melamine degradation. The peaks at 3055 and 3150 cm^{-1} which are representative of NH_3 show the highest intensities in the spectrum of the MEL(5%) + APP3 sample since it is a degradation product for both of them. However, all other peaks showed lower intensity compared with the SPE-PA-Ref spectrum except for the peak's representative of CO_2 . This phenomenon might be explained by the glowing of the

formed char as it is irradiated by a high-energy laser beam, which can catalyze the full oxidation of degradation products in the gas phase.

Gram-Schmidt curves which are shown in Figure 11 can represent the amount of evolved gases during the pyrolysis time of the samples.²⁵ It can be seen that SPE-SB-Ref and SPE-PA-Ref samples release the highest amount of pyrolysis gases; however, SPE-SB-Ref samples showed higher peaks at shorter times. SPE-WB-Ref and SPE-PA-Ref samples showed a small peak at the beginning which might be explained by water evaporation. The addition of APP and MEL to the SPE-PA system reduces the amount of the evolved gases, and adding them together shows the lowest Gram-Schmidt intensity due to the enhanced barrier effect of the intumescent char.

4 | CONCLUSION

Phytic acid (PA) was used as a reactive FR to prepare a fully water-borne biobased flame-retarded epoxy system since it can react with the epoxy groups of the sorbitol polyglycidyl ether epoxy monomer. It can be stated that phytic acid can promote the charring effect and reduce the release rate of both heat and gas-phase degradation products compared with solventborne and waterborne SPE systems; however, the lack of foaming agent in the system led to relatively low LOI values and HB UL-94 rate, but still higher than SPE-SB-Ref and SPE-WB-Ref systems.

When 5% melamine was used as a blowing agent, the char yield improved by 11%. When APP was added, both APP3 and MEL(5%) + APP3 samples showed almost twice the char yield compared with the SPE-PA-Ref sample. MEL(5%) + APP3 sample presents an increase in chare yield by 345.3% compared with the SPE-SB-Ref sample and 578.6% compared with the SPE-WB-Ref sample. In terms of flammability tests, the addition of melamine alone resulted in

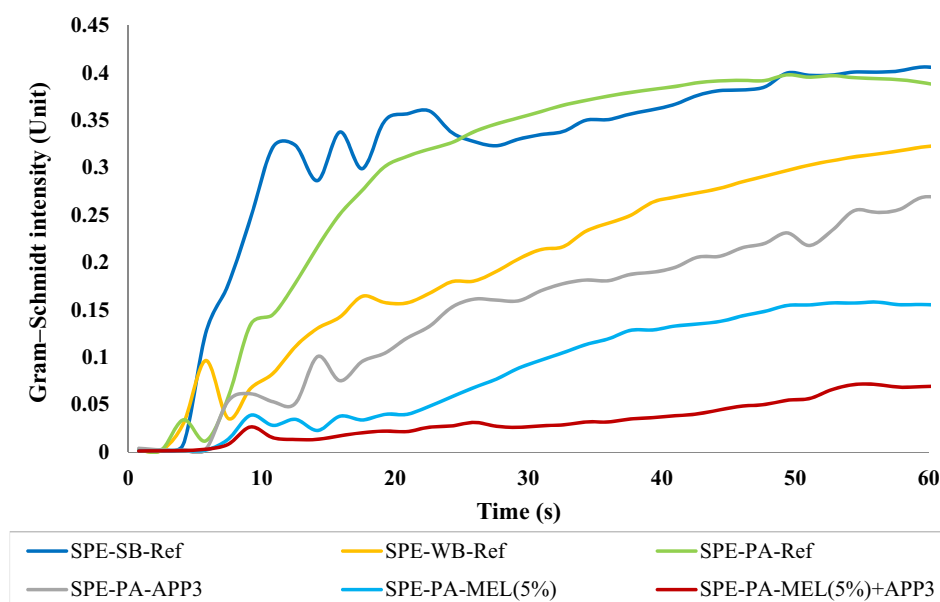


FIGURE 11 Gram-Schmidt values as a function of time during laser pyrolysis of SPE reference, APP, and MEL samples.

improved LOI values and V-1 UL-94 rating. Together with APP, LOI values of >50 V/V% were reached, indicating excellent flame-retardant performance.

The charring effect of phytic acid was confirmed by the extremely high time to ignition in MLC measurements compared with solvent-borne and waterborne SPE systems since a char layer was formed even before the ignition because of the dehydration of PA.

The flame-retardant effect of phytic acid can be indicated by the decrease of HRR from the burning samples. The SPE-PA-Ref sample presents a decrease in pHRR by 42.3% compared with the SPE-SB-Ref sample, and 30.1% compared with the SPE-WB-Ref sample. It also presents a decrease in THR by 24.6% compared with the SPE-SB-Ref sample, and 30.1% compared with the SPE-WB-Ref sample.

The intumescent effect was improved further by using MEL and APP. The sample MEL(5%) + APP3 showed the lowest pHRR and THR values, they decreased by 80.8% and 80.9% compared with the solventborne system, respectively. This might be explained by the formation of a less compact but spongier intumescent layer due to the presence of more mini pores in the char structure that can act to protect the inner material. Those pores can be seen in SEM images, while APP presents a more compact char with a smoother surface.

Although the addition of melamine with APP decreases the heat release during combustion, it leads to adhesive failure of the coating char of steel plates subjected to a 1-hour-long heat exposure after a certain time. In other words, the heat insulation properties of the intumescent coating deteriorated since the char photos showed that the cohesion and adherence of the char on the steel plate were weakened due to the extreme swelling performance of melamine. However, using PA as a curing agent together with APP decreased the final back-side temperature by 130°C compared with the solventborne sample and the steel temperature remained lower than the fracture temperature even after 1 h of heat exposure of 25 kW/m² of heat flux in MLC.

The mode of action of the applied FR composition was investigated by FTIR analyses of the charred residues and gas-phase degradation products. The ATR-IR spectrum of SPE-PA-Ref char showed that PA can promote the formation of carbonaceous char rich with P-species. The addition of APP increased the formation of ultra-phosphates in the char because of dehydration reactions within the epoxy matrix initiated by the phosphate groups; as a result, the intensities of peaks representative of P-species increased. FTIR spectra of laser pyrolysis products prove that with the use of phytic acid as a curing agent, the presence of phosphorous is obvious also in the gas phase, but in insignificantly lower amount than in the solid char. When APP was used, the intensity of the peaks decreased, and the lowest intensities were observed when melamine was added with APP, because of the rapid barrier effect of the formed char that was shown by Gram-Schmidt curves of the evolved gases during the pyrolysis time of the samples.

Accordingly, phytic acid proved to be a suitable curing agent for waterborne epoxy resins, leading to decreased flammability. Although to reach a V-0 rating, the addition of APP was needed, the flame-retardant effect of PA was presented both in the gas and solid phase, indicating its multi-functionality.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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