



# Investigation of the modes of action for phosphorous flame retardants in a fully waterborne sugar-based epoxy resin

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## Abstract

A fully waterborne epoxy system was prepared from waterborne sorbitol-based epoxy resin cured with an alkylated polyalkylene polyamine hardener. The flame-retardant property was accomplished by the application of different additive phosphorous flame retardants (FRs). Phosphonate polyol and ethyl ethylene glycol phosphate which are in the liquid phase, and two FRs in the form of fine-grained particles; aluminium diethyl phosphinate (AlPi), ammonium polyphosphate (APP). The flame-retardant epoxy resin blends were prepared at the same levels of phosphorus content. The results are very promising as the self-extinguishing behaviour was observed at 3%P for all the investigated FRs and at 1%P in the case of APP. Limiting oxygen index (LOI) values were practically good for all FRs and extremely improved in the case of APP. LOI was 48% for the APP sample at 3%P content. Furthermore, this blend showed the best results in the forced flaming conditions as the total heat release in cone calorimetry measurements (THR) decreased by 43% and the peak of heat release rate (pHRR) decreased by 65% with more elongated burning compared to the reference SPE matrix. The efficient solid-phase FR effect of APP was confirmed by scanning electron microscopic (SEM) and attenuated total reflection-infrared spectrometry (ATR-IR) analysis of the residual char after cone calorimetry measurements.

**Keywords** Waterborne epoxy system · Sorbitol-based bio-epoxy · Flame retardants · Phosphate · Phosphinate · Phosphonate

## Introduction

Epoxy resins are widely used in electric systems, coatings, adhesives, composites, and aerospace applications due to their exceptional properties. Currently, the industrial trends in production favour the replacement of organic solvents towards greener chemical processes, which can be accomplished by the utilisation of aqueous systems [1]. Waterborne epoxy resin systems have got increasing attention due to their good chemical resistance and adhesion [2]. However, they have some drawbacks like the shorter pot life and the dependency of drying and curing performance on the evaporation rate of water, which might be problematic in moist and cold environments [3]. Various research and application

prospects have been demonstrated for waterborne bio-based epoxy systems [4, 5]. In some applications of waterborne epoxy systems, waterborne epoxy curing agents can be used directly with solvent-based epoxy resins. However, these semi-solvent semi-aqueous systems have lower performance compared to the all-waterborne system [2].

Another environmentally benign perspective is the utilisation of bio-based polymers. The utilization of bio-based epoxy resins is strongly encouraged, as a result, considerable improvements have been achieved in the properties of bio-based epoxy resins to obtain performances comparable to petroleum-based ones [6]. However, bio-based waterborne epoxy systems with excellent flame-retardancy were seldom reported. Bio-epoxies derived from isosorbide have been studied and suggested as an excellent alternative for petroleum-based epoxies due to their rigid organic diol structure which has a similar reactivity with the widely used bisphenol-A epoxy resin (DGEBA) [7]. Another sugar-based bio-epoxy is sorbitol polyglycidyl ether, it is widely used due to its high functionality, which enhances crosslinking density and improves the system performance for many applications

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like coatings, adhesives, and electrical insulations [8]. To the best of our knowledge, waterborne epoxy systems based on sorbitol glycidyl ethers are not studied yet as a flame-retardant epoxy matrix.

Recently, polyoxypropylene amines have achieved a strong position in the market of epoxy curing agents [9]. The movability of C–O–C bonds existing in its structure provides more flexibility, this property is beneficial to relax the internal stress within epoxy resins cured at high temperatures [10].

Flame retardants are widely used in polymer composites to protect them against fire. These additives can effectively reduce the damage to people lives and property [11]. Phosphorus-containing compounds are very promising alternatives for halogen-containing flame-retardants in the market. They can act in the condensed phase or the gas phase or both, the mode of action depends on the flame-retardant composition and the possible interactions during combustion within the other components of the polymer system [12]. During thermal decomposition, the major amount of phosphorus in the system is oxidized to form phosphorus pentoxide ( $P_2O_5$ ) which tend to remove water from its surrounding and as result polyphosphoric acid ( $H_xP_yO_z$ ) will be formed, this acid is necessary to form the char in polymer systems containing phosphorus FRs [13].

It is almost generally accepted that phosphorus FRs are significantly more effective in oxygen- or nitrogen-containing polymers. The cured epoxy resins have a high concentration of OH groups, which react easily with phosphorus-containing products, leading to improved efficiency of the flame retardant [14]. Accordingly, the presence of water in the cured waterborne epoxy systems might present enhanced flame retardancy.

It has been demonstrated that the efficiency and the mode of action for aluminium diethyl phosphinate (AlPi) are dependent on the applied polymer system, but it mainly acts in the gas phase [15]. A loading of 15% AlPi into diglycidyl ether of bisphenol A (DGEBA) epoxy resin has displayed a self-extinguishing behaviour [16]. On the other hand, phosphate ester flame retardants can act both in the solid phase and the gas phase [17], while ammonium polyphosphate (APP) displays excellent activity in the solid phase. It has been used widely in intumescent flame-retardant systems for epoxy resins [18]. APP has been used with resorcinol bis(diphenyl phosphate) (RDP) as flame retardants for a solvent-borne SPE system. The blends which contain RDP (2% P) with APP (1% P) have displayed the self-extinguishing UL-94 rating and 34% LOI [19].

To the best of our knowledge, the only used phosphorus FRs for waterborne epoxy systems are 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and APP. They showed good flame retardant properties, but they have been used always in combination with other FRs. In this study, the

effect of different additive phosphorus flame retardants on the thermal and flame-retardant properties of a fully waterborne SPE epoxy system has been assessed. The flame retardancy mechanisms for the used FRs have been discussed by SEM, LP-FTIR and ATR-IR analysis.

## Materials and methods

### Materials

ERYSIS GE-61, a commercially available water-soluble sorbitol polyglycidyl ether (SPE), was obtained from Emerald Performance Materials (New Jersey, USA), epoxy equivalent mass: 160–195 g mol<sup>-1</sup>, viscosity at 25 °C: 4–7 Pa s.

Anquamine 401, an alkylated polyalkylene polyamine polymer, was acquired from Evonik Industries (Essen, Germany), the main component: polyoxypropylenediamine, amine hydrogen equivalent: 200 g equivalent, viscosity at 25 °C: 30 Pa s, Nonvolatile content: 70%.

Different additive FRs were used. Exolit OP560, a phosphonate polyol (P-content: 10–13%, density at 25 °C: 1.20 g cm<sup>-3</sup>, viscosity at 25 °C: 500 mPa s) supplied by Clariant International Ltd. RFL2.2 T, an oligomeric ethyl ethylene glycol phosphate (P-content: 19%) supplied by KhaiEL. Korea. Exolit OP945, a fine-grained aluminium diethyl phosphinate (AlPi) powder (P-content: 23.3–24.0%, average particle size  $\leq 5 \mu\text{m}$ ) supplied by Clariant International Ltd. Exolit AP422, a non-hygroscopic, a fine-grained phase II-ammoniumpolyphosphate white powder (P-content: 31–32%, average particle size of approximately 17  $\mu\text{m}$ ) supplied by Clariant International Ltd.

### Methods

#### Sample preparation

To produce the fully waterborne sorbitol polyglycidyl ether (SPE) matrix, the mixing ratio of ERYSES GE-61 and Anquamine 401 was 1:0.75. Anquamine 401 was diluted with half of its mass of distilled water to reduce the viscosity. The samples were cured in appropriate silicone moulds with standard sizes at 25 °C for 7 days. The adequate crosslinking of the samples can be demonstrated by the structural stability and gloss characteristics of the smooth surface. The flame-retardant epoxy samples were prepared at 1%, 2%, and 3% of phosphorus contents according to the phosphorus mass percent of each FR.

#### Thermogravimetric analysis (TGA)

TGA was conducted with a TA Q5000 device from TA Instruments. The sample mass was about 5 mg, and the

measurements were performed in the temperature range of 25–600 °C at a heating rate of 10 °C min<sup>-1</sup> using a Platinum-HT sample pan under nitrogen gas with a flow rate of 25 mL min<sup>-1</sup>.

### Characterization of fire behaviour

Limiting oxygen index measurements were carried out to measure the lowest concentration of oxygen that sustain the combustion of the sample in a candle-like setup (ASTM D-2863, sample dimensions: 120 mm × 15 mm × 4 mm).

The standard horizontal and vertical UL-94 flammability tests were carried out (according to ISO 9772 and ISO 9773, respectively) to assess the flammability of the reference and flame-retardant samples. A bunsen burner fire is applied to samples with the dimensions (120 × 15 × 4) mm and the classifications are as follows: HB (no fire extinguishing in the horizontal burning or dripping in the vertical burning), V-2 (flame extinguishment in the vertical burning within 30 s with dripping), V-1 (flame extinguishment in the vertical burning within 30 s and dripping is not allowed), V-0 (flame extinguishment in the vertical burning within 10 s and dripping is not allowed).

A mass loss type cone calorimeter (FTT Inc instrument) following ISO 13927 standard method was used to study burning behaviour. Specimens with approximate dimensions of (100 × 100 × 2) mm were exposed to an external heat flux of 25 kW m<sup>-2</sup> and the combustion was initiated by an igniter. The burning behaviour was characterized by different measures: the time to ignition (TTI) indicates the ease of ignition while heat release rate (HRR), peak heat release rate (pHRR) and time to the peak heat release rate determines the flame spread, and the total heat released (THR) corresponds to the fire load. These values are generally used to determine the efficiency of flame retardants.

### Scanning electron microscopy (SEM)

The microstructure of the residual char after MLC measurements was analysed by scanning electron microscopy. The char was coated with a golden layer and the micrographs were obtained at 15 keV accelerating voltage by JEOL JSM-5500 scanning electron microscope (JEOL Ltd., Tokyo, Japan).

### Attenuated total reflection infrared (ATR-IR) analysis

The charred residues after mass loss type cone calorimeter (MLC) measurements were analysed in a wavenumber region of 4000–600 cm<sup>-1</sup> by IR spectra in ATR mode using Bruker Tensor 37 FTIR spectrometer (Billerica, USA) equipped with a Spec Ac Golden Gate ATR.

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

To investigate the possible gas-phase effect of the different flame retardants, the pyrolytic degradation products of reference and FR samples were analysed by a coupled LP-FTIR analysis. The CO<sub>2</sub> pyrolyser laser unit (10.6 nm, SYNRAD 48–1, Mukilteo, USA) was coupled with the same Bruker Tensor 37 FTIR spectrometer to analyse the pyrolysis gases instantaneously. The applied laser power for the pyrolysis of the samples was 1 W for 1 min.

## Results and discussion

### Thermogravimetric Analysis (TGA)

TGA measurements determine the thermal stability of the reference and flame-retardant samples. Table 1 shows

**Table 1** TGA results of references and flame retarded samples

FR composition	T <sub>-10%</sub> /°C	T <sub>-50%</sub> /°C	dTG <sub>max</sub> /%/°C <sup>-1</sup>	T <sub>dTGmax</sub> /°C	Char yield/%
SPE reference (0%P)	253.8	331.2	1.13	302.1	9.9
Phosphonate polyol (1%P)	235.8	319.5	1.34	305.4	16.5
Phosphonate polyol (2%P)	220.3	317.1	1.13	303.9	15.6
Phosphonate polyol (3%P)	179.2	313.3	0.88	298.4	13.3
Alkyl phosphate (1%P)	271.6	323.3	1.41	304.2	14.6
Alkyl phosphate (2%P)	262.9	319.9	1.28	299.4	18.0
Alkyl phosphate (3%P)	258.9	320.0	1.14	300.2	18.4
AlPi (1%P)	268.9	335.3	0.98	308.8	18.4
AlPi (2%P)	268.1	342.5	0.89	311.1	17.3
AlPi (3%P)	267.0	350.7	0.86	319.2	21.6
APP (1%P)	265.9	320.5	1.26	308.9	22.4
APP (2%P)	269.8	322.9	1.24	309.1	24.4
APP (3%P)	265.0	329.6	1.07	308.6	29.3

different measures of TGA: the temperature at 10% and 50% mass loss, ( $T_{-10\%}$ ;  $T_{-50\%}$ ), the maximum mass loss rate ( $dTG_{max}$ ), the temperature at the maximum mass loss rate ( $T_{dTGmax}$ ) and the char yield at 600 °C.

However, the addition of FRs might affect the thermal degradation behaviour of the cured epoxy. It can be seen from  $T_{-50\%}$  values that the introduction of FRs reduced the thermal stability of the waterborne epoxy, this might be explained by the catalytic effect of phosphoric acid produced by the thermal degradation of epoxy systems containing phosphorous FRs [20]. The decrease in the  $T_{-50\%}$  of the phosphonate polyol flame retardant is explained by its chemical structure. It is found that dissociation of a P-O bond (90 kcal mol<sup>-1</sup>) requires more energy than dissociation of an O-C (85.5 kcal mol<sup>-1</sup>) or P-C (70 kcal mol<sup>-1</sup>) bond, and Phosphonate polyol contains more O-C and P-C bonds that can break easier than other FRs [21]. The presence of aliphatic chains in its structure also decreases thermal stability.

TG curves for neat epoxy resin and FR blends with 3%P content of flame retardants are illustrated in Fig. 1.

It can be seen from the TG curves in Fig. 1 that before the main degradation step there is a small loss in the sample mass due to the evaporation of water (around 5–7%). SPE reference system showed two steps of degradation. The epoxy matrix undergoes a more rapid mass reduction in the first step (up to approximately 340 °C) compared to the second step. The mass loss in the first degradation step might be attributed to some dehydration and elimination reactions on the epoxy chains at the beginning, followed by chain scission and fragmentation reactions, as a result, some carbonaceous char was formed. This char decomposed in the second

thermal degradation step of the system (between 340 °C and 420 °C). The relatively small difference in mass loss rate between the first and second degradation steps indicates that the formed char was very weak. This might be explained by the presence of aliphatic chains in the SPE structure and the alkylated polyalkylene polyamine curing agent.

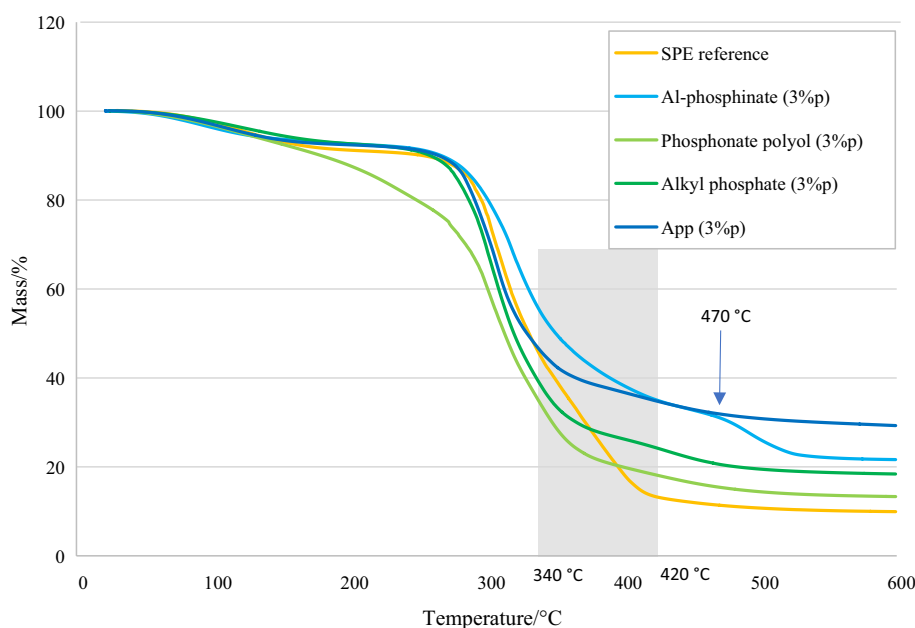
It can be observed from Table 1 that the onset temperatures of degradation for all FR samples were higher than in the case of the reference sample except for phosphonate polyol. Moreover, in this case, the small initial mass reduction step ascribed to the evaporation of water from the system cannot be separated from the degradation process like in the case of other FR samples, and no significant changes were observed before the main degradation step, whereby, the sample lost 25% of its mass due to the high -OH content which was targeted by the dehydration reactions. As a result, a reduction in char yield by increasing the phosphonate polyol content can be detected.

The lower thermal stability observed in the case of phosphonate polyol and alkyl phosphate samples shown in Fig. 1 might be explained by the relatively low stability of phosphorus ester bonds in the flame retardant formulation [22], furthermore, the formed char is weaker than in the case of AlPi and APP samples as it decomposes at lower temperatures.

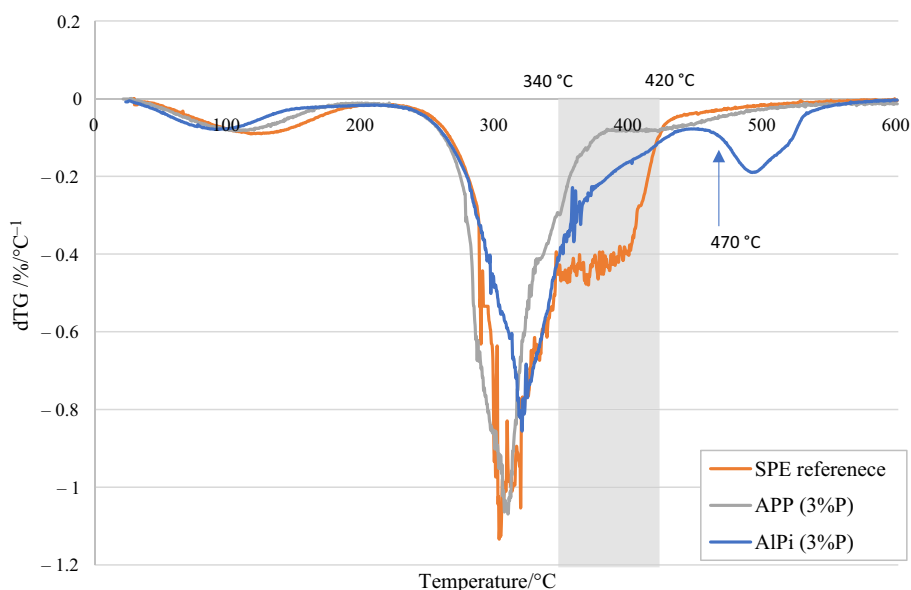
Even though AlPi samples showed higher degradation temperatures, the formed char is weaker than in case of APP samples. The char formed in case of AlPi (3%P) sample decomposed at around 470 °C leading to a lower residual char mass (Fig. 1 and Fig. 2).

It can be noted from the TGA curves in Fig. 1 and dTG curves in Fig. 2 that APP starts its activity in the solid phase

**Fig. 1** TGA curves in the range of 25–600 °C of the SPE reference and flame retarded samples at 3%P content under nitrogen (heating rate 10 °C min<sup>-1</sup>)



**Fig. 2** dTG curves in the range of 25–600 °C of the SPE reference, AlPi (3%P), and APP (3%P) under nitrogen (heating rate 10 °C min<sup>-1</sup>)



at the beginning of the second degradation step of the system as the slope of the TG curve representing APP (3%P) sample in Fig. 1 a indicates better thermal stability of the formed char, and this can be very beneficial at bigger sizes. It can be seen from the dTG curves in Fig. 2 how the mass loss rate decreases very significantly at this stage due to the formation of a char which is almost stable until 600 °C. This observation strongly nominates APP as the most suitable FR for the waterborne SPE epoxy matrix among the investigated FRs.

### Limiting Oxygen Index (LOI) and UL-94 Standard results

The flammability of the reference and FR samples was determined by UL-94 and LOI tests. Their results are summarized in Table 2.

It can be determined from Table 2 that the reference SPE system showed the lowest LOI (22%) and the least flammability rating (HB) according to UL-94 measurements, which indicate the inherent flammability.

However, the addition of any of the used flame retardants increased the LOI values to be conformed with the standards which stated that LOI should be higher than 27–29% [23]. According to the results, phosphonate polyol and alkyl phosphate samples showed very close LOI values, but the UL-94 ratings were higher in the case of alkyl phosphate as it showed a V-0 rating at only 2%P and V-1 rating at 1%P while phosphonate polyol could not stop vertical flame spread at 1%P content and displayed HB rating.

AlPi samples also showed the self-extinguishing rating V-0 at 2%P, but lower LOI at 1%P and 2%P compared to those of phosphonate polyol and alkyl phosphate samples. APP samples showed the best results as they showed a V-0

**Table 2** LOI and UL-94 results of the reference sample and flame retarded formulations

FR composition	LOI/%	UL-94 rate
SPE reference (0%P)	22	HB (22.7 mm min <sup>-1</sup> )
Phosphonate polyol (1%P)	31	V-1 (burning time 23 s)
Phosphonate polyol (2%P)	33	V-1 (burning time 11 s)
Phosphonate polyol (3%P)	34	V-0
Alkyl phosphate (1%P)	32	V-1 (burning time 13 s)
Alkyl phosphate (2%P)	33	V-0
Alkyl phosphate (3%P)	33	V-0
AlPi (1%P)	26	V-1 (burning time 13 s)
AlPi (2%P)	29	V-0
AlPi (3%P)	34	V-0
APP (1%P)	32	V-0
APP (2%P)	41	V-0
APP (3%P)	48	V-0

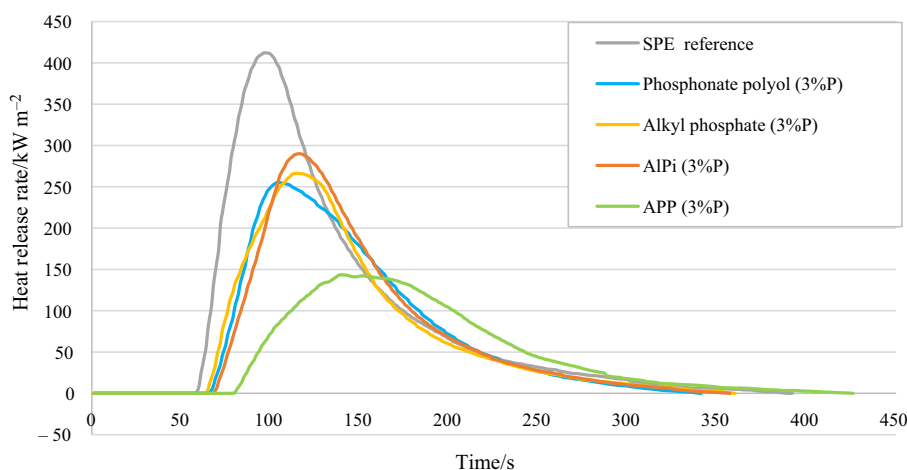
UL-94 rating even at 1%P content due to the formation of highly intumescent char which can effectively protect the underlying material by hindering the oxygen and heat exchange. This can also explain the significantly high LOI values (48% at 3%P), which is an extraordinarily high value for epoxy systems.

### Mass loss calorimetry results

Cone calorimeter results of the reference and FR samples at different P-contents are summarised in Table 3. Heat release rate (HRR) curves for the reference and 3%P flame retarded samples at 25 kW m<sup>-2</sup> heat flux are shown in Fig. 3.

**Table 3** Mass loss calorimetry results of reference and flame retarded samples

FR composition	TTI/s	pHRR/kW m <sup>-2</sup>	Time of pHRR/s	THR/MJ m <sup>-2</sup>	FIGRA/kW m <sup>-2</sup> s	Residue/mass%
SPE reference (0%P)	58	412	97	33.4	4.2	2.2
Phosphonate polyol (1%P)	62	367	106	28.5	3.5	3.7
Phosphonate polyol (2%P)	63	296	106	21.8	2.8	6.3
Phosphonate polyol (3%P)	65	256	104	24.9	2.5	9.2
Alkyl phosphate (1%P)	63	336	108	27.5	3.1	4.9
Alkyl phosphate (2%P)	63	299	112	26.2	2.7	8.2
Alkyl phosphate (3%P)	64	266	115	24.7	2.3	8.1
AlPi (1%P)	58	397	105	32.8	3.8	5.8
AlPi (2%P)	59	357	99	27.9	3.6	9.5
AlPi (3%P)	68	290	116	25.2	2.5	11.5
APP (1%P)	60	229	112	21.4	2.0	21.5
APP (2%P)	64	183	132	21.0	1.4	22.6
APP (3%P)	79	144	140	19.1	1.0	23.8

**Fig. 3** Heat release rate (HRR) for a heat flux of 25 kW m<sup>-2</sup> of SPE reference sample and FR (3%P) samples

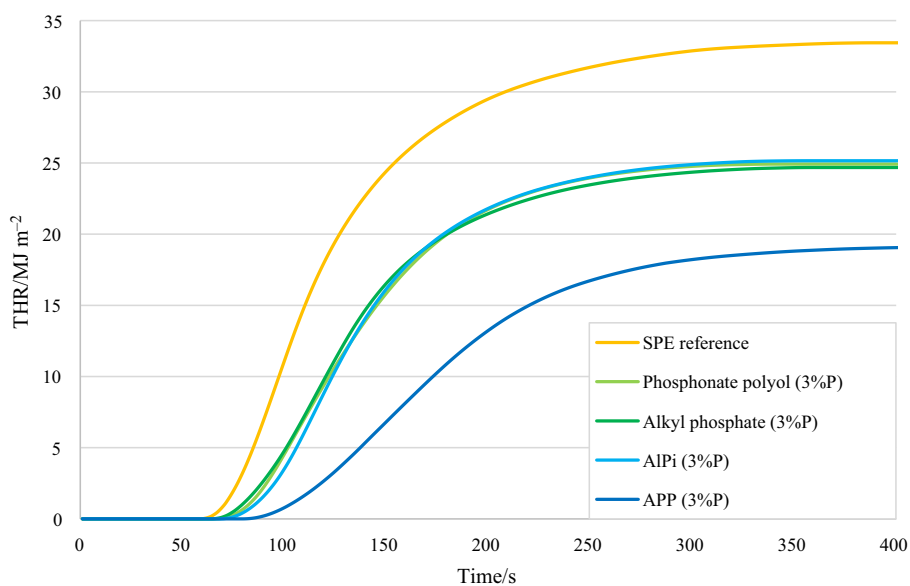
The fire behaviour assessment by cone calorimetry results can give a comprehensive understanding in terms of the propensity of the material to undergo a quick growing fire and burn for a relatively long duration. It can be seen from Table 3 that the time to ignition (TTI) increased when FRs were added by and by increasing phosphorous content indicating the activity of flame retardants in delaying the ignition of the epoxy matrix [24].

Heat release rates obtained by mass loss calorimetry are important to understand the changes in the fire behaviour of the system due to the addition of FRs, mainly the total heat release (THR) and the peak of heat release (pHRR) are very considerable parameters to evaluate the fire safety of the material [24]. It can be stated from Table 3 that the reference SPE system burned with relatively high HRR and lost 97.8% of its mass, leaving almost no residue. However, all flame retarded samples exhibited a significant reduction of both pHRR and THR along with an increase in char yield. The

accompanying shift in time of pHRR was expressed by fire growth rate (FIGRA = pHRR/ time of pHRR). The reduction in FIGRA values by using FRs and increasing P-content also indicates the development of flame retarding properties.

It can be concluded from Table 1, Fig. 3, and Fig. 4 that the heat release results of phosphonate polyol and alkyl phosphate (3%P) blends are very close to each other. A minor increase in heat release is noticed in the case of the AlPi (3%P) sample. In the case of the phosphonate polyol (3%P) sample, the pHRR decreased by 38% (from 412 to 256 kW m<sup>-2</sup>) and the THR decreased by 26% (from 33.4 to 24.9 MJ m<sup>-2</sup>). Whereas, in the alkyl phosphate samples at 3%P content, the pHRR decreased by 36% (from 412 to 266 kW m<sup>-2</sup>) and the THR decreased by 26% (from 33.4 to 24.7 MJ m<sup>-2</sup>) compared to the reference SPE matrix. The residual char yields for phosphonate polyol and alkyl phosphate blends were lower than in the case of AlPi samples due to the partial oxidation of phosphinate to phosphate structure

**Fig. 4** Comparison of the total heat release (THR) of the reference SPE sample and FR (3%P) samples



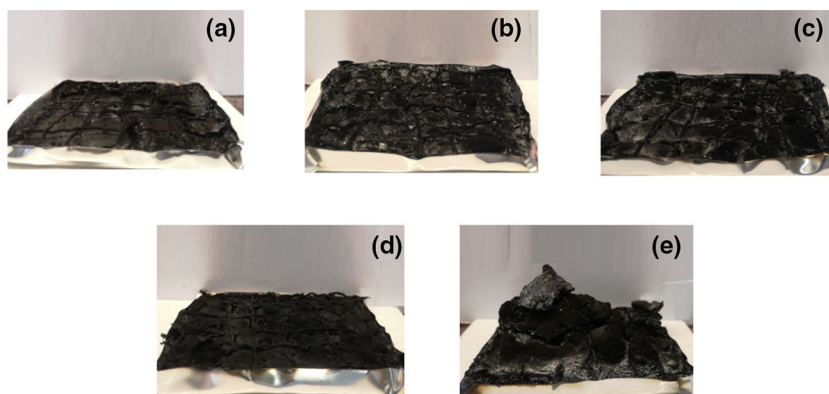
during combustion, despite that, AlPi samples showed higher THR and pHRR, due to the insufficient barrier effect of the formed char leading to more decomposition of the underlying material. However, the higher TTI values for AlPi might be explained by the gas-phase effect of phosphinate-type flame retardants as they partially decomposed to volatile phosphorous radicals that act as flame inhibitors by reacting with the radicals formed in the combustion zone which might delay the ignition [15].

APP samples displayed the best results among the used FRs. At 3%P content, THR decreased by 43% (from 33.4 to 19.1 MJ m<sup>-2</sup>) and pHRR decreased dramatically by 65% (from 412 to 144 kW m<sup>-2</sup>) with more elongated burning as the time to reach pHRR increased by 43 s (from 97 to 140 s) compared to the reference SPE matrix. APP decomposes during combustion to form polyphosphoric acid and ammonia. Polyphosphoric acid reacts with OH groups of

the cured epoxy resin to produce phosphate esters [25]. At high temperatures, the dehydration and crosslinking reactions of phosphate esters will lead to the formation of an intumescent char layer which can act as a heat shield and significantly decrease HRR [19].

Photos of the char residues after the cone calorimetry test for the flame-retardant samples containing 3%P are illustrated in Fig. 5. The reference SPE sample exhibited low char yield due to the high flammability. However, with the addition of flame retardants and increasing phosphorus content, the char became denser and more continuous, so it provided a better shield to protect the underlying material from the heat source. This effect has been shown before in the development of UL-94 ratings and increasing LOI values by increasing P content. The charring effect was more evident in the case of APP samples since thicker char and higher char yields were observed.

**Fig. 5** Digital photos of the char residues for the samples: **A.** Reference SPE, **B.** Phosphonate polyol (3%P), **C.** Alkyl phosphate (3%P), **D.** AlPi (3%P), **E.** APP (3%P) after cone calorimetry with a heat flux of 25 kW m<sup>-2</sup>



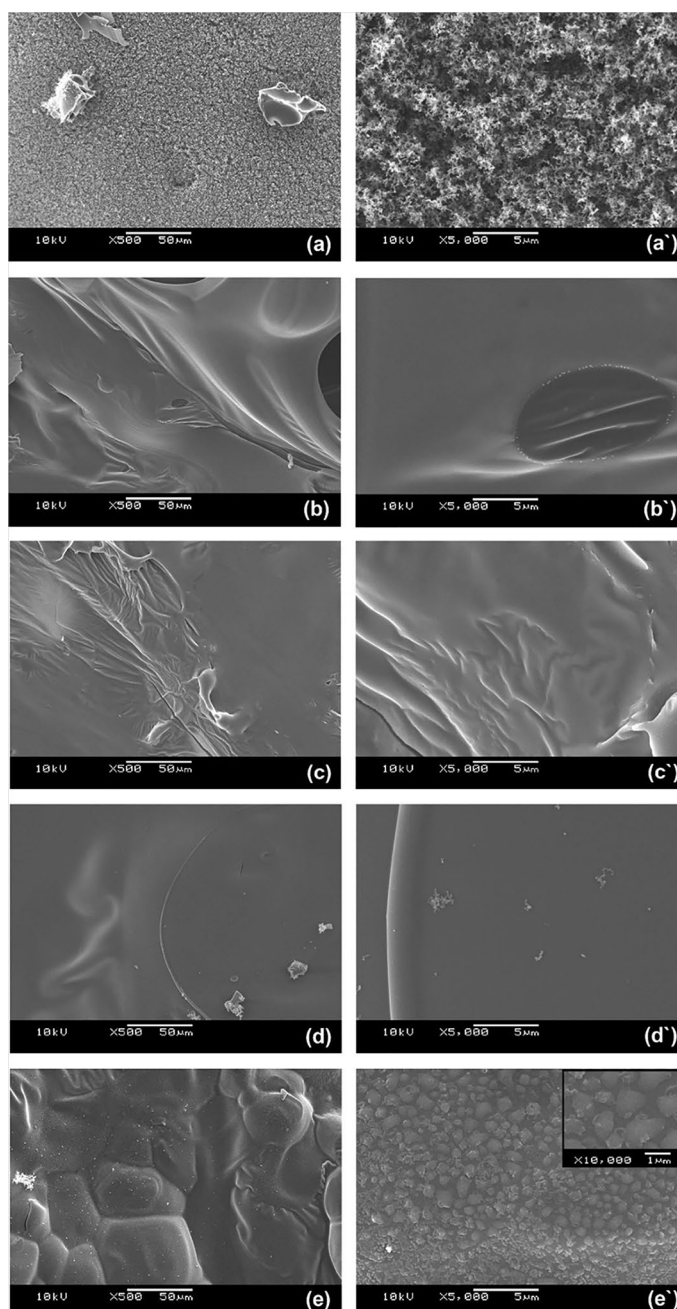
## Scanning electron microscopy (SEM)

The solid phase effect for the used FRs can be discussed further by comparing the char structure characterized by scanning electron microscopy [26]. The morphology for the MLC residual char is shown in Fig. 6.

The char of the reference SPE sample (Fig. 6. a, a') has a porous structure, which can explain the high HRR values compared with the FR samples which showed a more continuous char surface. In the case of phosphonate polyol char, bigger holes were observed (Fig. 6. b). Those holes were

formed during the expansion of the formed char, reducing the mass and heat insulation effect of the char. At higher magnification, it can be seen in figure b' weak point in the char surface which can turn into a hole at further char expansion. No such holes were observed for the other samples. In the case of alkyl phosphate (Fig. 6. c, c') some cracks were shown on the char surface, which decreased the efficiency of the intumescent char. The char yield in the case of the AIPi sample was slightly higher than phosphonate polyol and alkyl phosphate samples, however, the HRR values were higher (Table 3). This might be explained by the

**Fig. 6** SEM images of the MLC char at  $\times 500$  and at  $\times 5000$  magnifications consequently for (a, a') SPE reference sample, (b, b') phosphonate polyol (3%P), (c, c') alkyl phosphate (3%P), (d, d') AIPi (3%P), and (e, e') APP (3%P)





thin and fragile char layer, with major cracks on the surface, although, at the microscopic level, the measured piece of char showed a continuous surface with minor cracks (Fig. 6. d, d'). APP samples produced the highest char yield and the lowest HRR values (Table 3). The formed char was thicker and more compact (Fig. 5). It can be seen in (Fig. 6. e) that the char is formed from closed cells, and these cells are made up of smaller cells (Fig. 6. e') which might be created by the intumescent effect since the char swelled by the released gases to produce a spongy structure, which has better heat isolation and better barrier effect for the combustible gases release [27].

### Attenuated total reflection-infrared spectrometry (ATR-IR) analysis of the solid residues

The char residues obtained from the samples in the mass loss calorimeter were analysed by ATR-IR, and their spectra are shown in Fig. 7.

It can be observed in Fig. 7 that the peaks which represent the char residues of the reference system include  $1560\text{ cm}^{-1}$  (aromatic C=C) and  $1200\text{ cm}^{-1}$  (C-O) [28]. In FR samples, there are some similar peaks compared to the reference system spectrum, however, some signals assigned to phosphorus species in the solid phase are traceable. It can be seen in Fig. 7 that the spectra of phosphonate polyol and alkyl phosphate are very similar. The observed peaks representative of phosphorus species are relatively small and located in the region  $1350\text{--}1150\text{ cm}^{-1}$  (P=O) and at around  $965\text{ cm}^{-1}$  (P-O-P group) [29], which indicates the formation

of ultraphosphate substances in the char layer, promoted by the dehydration of the epoxy matrix [30].

The most obvious peak for AlPi sample residues was at  $1075\text{ cm}^{-1}$  attributed to the phosphate structure due to the partial oxidation of the phosphinate during combustion, however, it showed a lower peak in the aromatic C=C range ( $1560\text{ cm}^{-1}$ ), since the activity of AlPi is more pronounced in the gas phase. However, in the case of the APP sample, broad peaks appear at around  $2780\text{ cm}^{-1}$  and  $2325\text{ cm}^{-1}$  characteristic of the P-OH groups, which indicate the formation of phosphoric acid during APP thermal degradation [29]. Peaks with higher intensity were observed in the region  $1050\text{--}855\text{ cm}^{-1}$  (P-O-C group) which are most probably generated from the esterification reaction between P-OH groups formed during the thermal decomposition of APP and OH groups of the epoxy resin [30]. The peak at  $1120\text{ cm}^{-1}$  indicates the presence of a phosphate structure. The very sharp peak observed at around  $965\text{ cm}^{-1}$  (P-O-P group) might be attributed to the formation of ultraphosphate because of APP's significant activity in the condensed phase [30]. The peak at around  $1585\text{ cm}^{-1}$  (aromatic C=C) presents higher intensity compared to other FRs, which demonstrates the higher charring effect of APP [29]. Therefore, it can be concluded that APP can promote the formation of P- and C-rich char with more aromatic content.

### Coupled laser pyrolysis-FTIR analysis of the gaseous phase

The activity of the used FRs in the gas phase was investigated using a laser pyrolysis-FTIR coupled method [31].

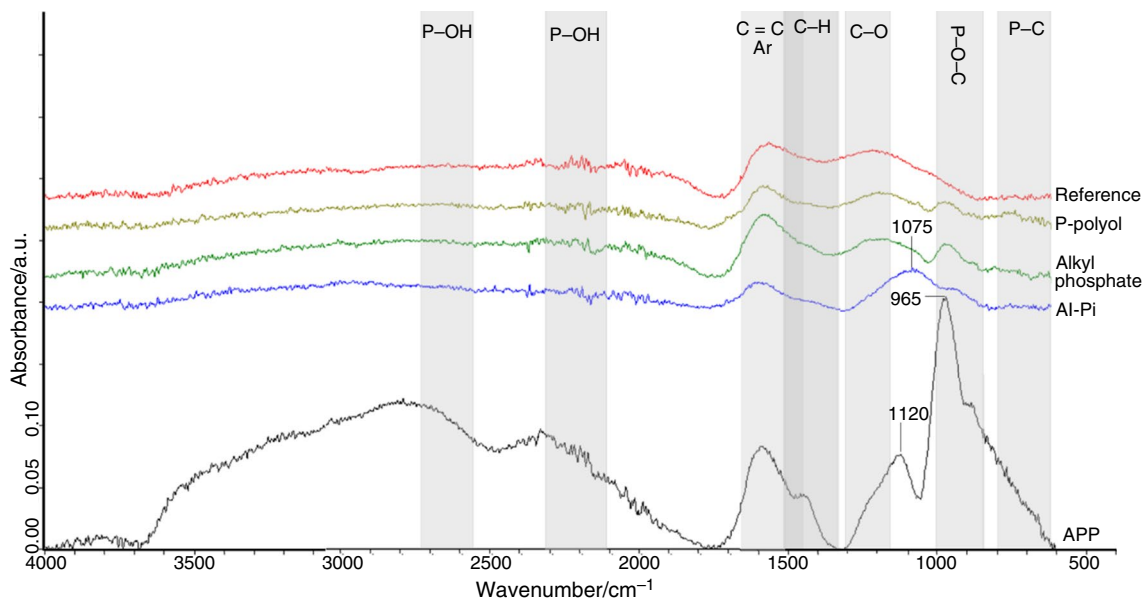
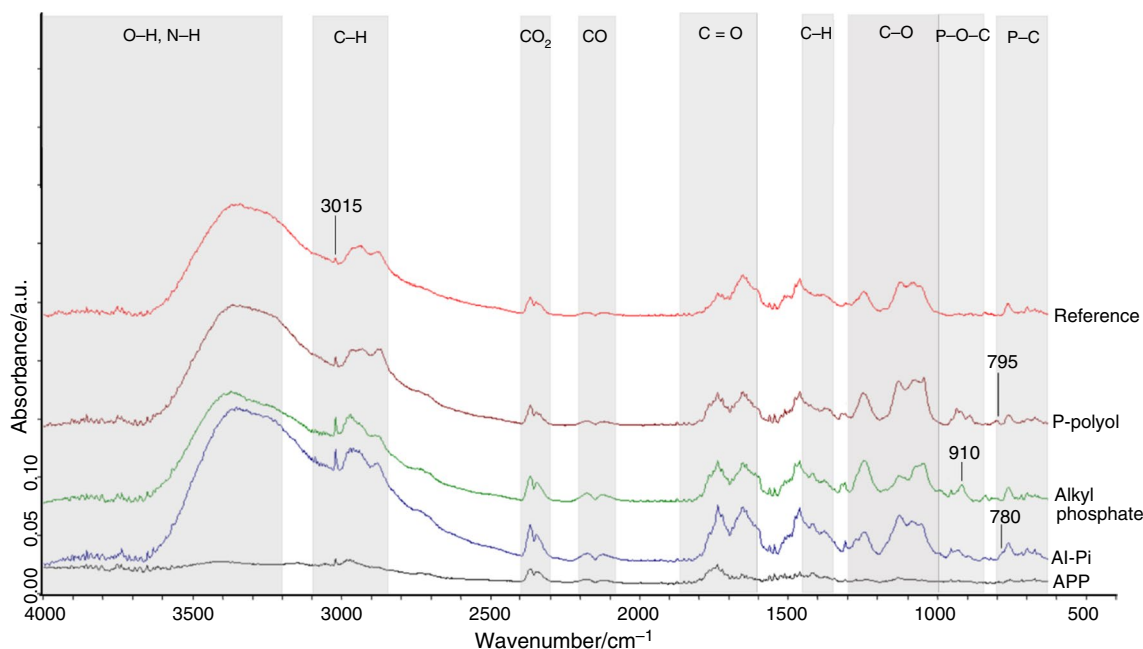


Fig. 7 ATR-IR spectra of the mass loss calorimeter charred residues for SPE reference and (3% P) FR samples



**Fig. 8** LP-FTIR spectra of the degradation products in the gas phase for the reference and P-containing samples

This method allows a fast way to determine the gas-phase decomposition products of the different samples. A high-energy  $\text{CO}_2$  laser is used to cause thermal degradation of the samples, while the formed gases are in situ analysed using the FTIR method. The FTIR spectra of the degradation products of the investigated samples are shown in Fig. 8.

According to Fig. 8, all samples showed peaks in the regions  $2400\text{--}2300\text{ cm}^{-1}$  ( $\text{CO}_2$ ), and  $2200\text{--}2080\text{ cm}^{-1}$  ( $\text{CO}$ ), and the peaks in the regions  $2963\text{--}2865, 1457\text{ cm}^{-1}$  which are characteristic of aliphatic hydrocarbons released in the gas phase due to the chain scission of the epoxy system [30]. Other peaks were observed in the regions  $1300\text{--}1000\text{ cm}^{-1}$  (C-O),  $1870\text{--}1550\text{ cm}^{-1}$  (C=O),  $3100\text{--}3000\text{ cm}^{-1}$  (C-H vibrations in aromatic and olefinic compounds),  $3015\text{ cm}^{-1}$  (methane), and  $4000\text{--}3200\text{ cm}^{-1}$  (O-H and N-H stretching due to the release of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ) [28], all of which are correlated with the decomposition of the cured epoxy matrix [17]. Many peaks for phosphorus species could be identified in the gas phase spectra of the different phosphorous FR formulations except for APP. The signals detected in the region  $1050\text{--}855\text{ cm}^{-1}$  (P-O-C group) and the peaks at around  $795\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  (P-C) were indicating the release of P species in the gas phase and therefore the flame inhibition activity of these FRs. Alkyl phosphonate and AlPi samples showed a peak at  $910\text{ cm}^{-1}$  attributed to P-O-P vibration) [29], which most probably formed as a result of the radical-scavenging effect of P radicals [32].

The intensity of the peaks representative for P-species in the gas phase increased in the order of decreasing the oxidation state of P in the flame retardant, from alkyl phosphate to

Phosphonate polyol and then AlPi, this might indicate that FRs with lower oxidation state present higher flame retardant activity in the gas phase. However, in the case of the APP sample, not only the peaks representative of P-species were missing, but also the peaks related to the degradation products of the epoxy matrix observed in the reference sample. Only the peak attributed to  $\text{CO}_2$  formation existed with comparable intensity. The explanation is that due to the high-energy laser beam, the char is formed very soon, and after it is glowing, the degradation products were oxidised as they are coming through this glowing char, which might be proof that APP has no significant gas-phase effect.

## Conclusions

In this work, fully waterborne flame-retardant bio-epoxy resin blends have been prepared with the addition of some phosphorous-based FRs. According to TGA measurements, higher char yield was produced in case of APP samples, and that char showed better thermal stability than other samples, which was also confirmed by the flame retardancy measurements. APP presented the self-extinguishing V-0 UL-94 rating at 1%P content, while in case of Al-phosphonate and alkyl phosphate 2%P content was needed, and 3%P of phosphonate polyol was needed to present the V-0 rating. The intumescent char of APP can effectively protect the underlying material by hindering the oxygen and heat exchange, which can explain the significantly high LOI values (48% at 3%P), and the low heat release under simulated

fire conditions in mass loss calorimetry measurements. APP sample at 3%P content showed THR decreased by 43% and pHRR decreased by 65% with more elongated burning compared to the reference SPE matrix.

In agreement with TGA results, the residual char yields for phosphonate polyol and alkyl phosphate blends were lower than in the case of AlPi samples, however, AlPi samples showed higher THR and pHRR, due to the insufficient barrier effect of the formed char, since it was thin and fragile with major cracks on the surface, although, at the microscopic level, the measured piece of char showed a continuous surface with minor cracks. Some micro-cracks were observed in the micrographs of the char surface for alkyl phosphate sample, which decreased the efficiency of the intumescent char. The charring effect was not sufficient even in the case of phosphonate polyol since relatively big holes were formed during the expansion of the formed char since it has lower thermal stability.

The results of LP-FTIR experiments demonstrated that P-species were released in the gas phase during the pyrolysis of the FR formulations to act as flame inhibitors, and the intensity of their spectra peaks increased in the order of decreasing P oxidation state of in the FR, from alkyl phosphate to Phosphonate polyol and then AlPi. However, the APP sample did not show peaks representative of P-species. On the other hand, the ATR-IR spectra observations confirmed that the presence of P-species “especially ultraphosphate” in the residual char increased by increasing the P oxidation state of the FR. APP presents significant activity in the condensed phase and can promote the formation of P- and C-rich char with more aromatic content. It can be seen in the char micrographs of APP sample that the char is formed from closed cells, which are made up of smaller cells created by the intumescent effect, since the char swelled by the released gases to produce a spongy structure, which has better heat isolation and better barrier effect for the combustible gases release.

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