



HAL
open science

Synthesis of biobased phosphate flame retardants

Raphael Ménard, Claire Negrell, Laurent Ferry, Rodolphe Sonnier, Ghislain David

► **To cite this version:**

Raphael Ménard, Claire Negrell, Laurent Ferry, Rodolphe Sonnier, Ghislain David. Synthesis of biobased phosphate flame retardants. *Pure and Applied Chemistry*, 2014, 86, pp.1637-1650. 10.1515/pac-2014-0703 . hal-01091373

HAL Id: hal-01091373

<https://hal.science/hal-01091373>

Submitted on 1 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Raphaël Ménard, Claire Negrell-Guirao, Laurent Ferry, Rodolphe Sonnier
and Ghislain David*

Synthesis of biobased phosphate flame retardants

Characterization of flame retardancy on epoxy thermosets

Abstract: An approach to prepare some biobased flame retardant (FR) compounds is presented. The adopted strategy consists in functionalizing an aromatic biobased phenolic compound, the phloroglucinol, with different phosphate groups in order to promote a charring effect. Different chlorophosphates were grafted onto phloroglucinol hydroxy groups and the functionalization of the hydroxy groups was quantitative. The synthesized biobased FR were incorporated into an epoxy matrix as additive to estimate their flame retardant properties. The influence of different parameters was studied such as the phosphorus content of the thermoset or the nature of the R group of the used phosphate P-O-R. MEB/EDX observations proved the influence of this R group on the compatibility between the FR and the matrix and its importance to obtain homogeneous thermoset. Thermogravimetric analyses of the phosphorus-containing thermosets showed a small decrease in thermal stability accompanied by a char yield almost tripled for a 3 %_wP-containing thermoset compared to that of the thermoset without any FR. Pyrolysis combustion flow calorimetry was also used to evaluate the flammability of the modified epoxy thermoset. A significant decrease in peak of heat release rate and total heat released was observed compared to thermoset without FR. These results demonstrate the good flame retardant properties of these biobased phosphates in an epoxy matrix. In addition these results show the potential of the biobased phenolic compounds as raw material for flame retardants syntheses.

Keywords: biobased flame retardants; epoxy networks; phosphorus-containing additives; POC-2014.

*Corresponding author: **Ghislain David**, Institut Charles Gerhardt, Montpellier, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France, e-mail: ghislain.david@enscm.fr

Raphaël Ménard: Institut Charles Gerhardt, Montpellier, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France; and Ecole des Mines d'Alès, Centre des Matériaux des Mines d'Alès – Pôle Matériaux Polymères Avancés, 6 Avenue de Clavières, 30319 Ales Cedex, France

Claire Negrell-Guirao: Institut Charles Gerhardt, Montpellier, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France

Laurent Ferry and Rodolphe Sonnier: Ecole des Mines d'Alès, Centre des Matériaux des Mines d'Alès – Pôle Matériaux Polymères Avancés, 6 Avenue de Clavières, 30319 Ales Cedex, France

Introduction

Epoxy resins are widely used for their characteristics, such as excellent mechanical properties, adhesion or thermal resistance and have many applications in adhesive industry, coatings, electronic components and materials for energy. The flammability of these resins is one of their main drawbacks and implies the systematic introduction of flame retardant compounds (FR) in their formulation.

Phosphorus-containing FRs are known for their different mechanisms that occur during burning. They can act in gas and/or in condensed phases. Phosphorus atoms promote charring and the char formed acts as a barrier against heat and gas (O_2 and pyrolysis gases). Their action in condensed phase appears as a key parameter of the fireproofing material. An additional mode-of-action is flame poisoning. Organophosphorus compounds used as additives represent an important part of flame retardant market [1] and are currently the most studied FRs mainly due to the restrictions of halogenated products imposed by REACH or RoHS regulations [2, 3]. It is likely to note that phosphorus FR release much less toxic compounds [4] than halogenated ones.

The mode-of-actions of phosphorus-containing FRs depend upon several parameters and most often the action in the condensed phase is preferred. The aromaticity of the FR structure promotes the char formation during the thermal decomposition. The oxidation state of the phosphorus atom is also a key parameter. Indeed, some studies [5, 6] showed that the higher the oxidation degree of phosphorus atom, the better the action in condensed phase. So, both phosphate and phosphonate are the most suitable phosphorus groups to promote charring during the thermal decomposition of the material.

Our previous study [7] achieved with phosphorus-containing oligomers allowed determining that an aliphatic FR used in an aromatic matrix led to a phase segregation which provides heterogeneous thermosets. Thus, the similarity between the FR and the matrix structure also appears as a key parameter to make available flame-retarded thermosets.

To the best of our knowledge, no biobased aromatic phosphorus-containing FR commercially available used in epoxy matrix [8, 9] has been reported so far. Some studies found in the literature describe the synthesis of biobased phosphorus-containing FRs: Ma et al. [10] used the itaconic acid as bio-based resource and grafted the 9,10-dihydro-9-oxo-10-phosphaphenanthrene-10-oxide (DOPO) onto the C=C bond to afford both aromaticity and phosphorus group. Lligadas et al. [11] also grafted the DOPO onto fatty acid derivative.

However, some biobased resources naturally show an aromatic structure. Phenolic products coming from the depolymerization of lignins exhibit the required aromatic structure and are easily available. Indeed, lignins are the second most abundant raw material in the nature and the most abundant aromatic polymer. These phenolic products can be modified by functionalizing their reactive groups as aldehydes, carboxylic acids or hydroxy groups and these last ones can easily be functionalized via a Williamson etherification [12]. Using the same reaction, these reactive functions can also be grafted with phosphorus-containing compounds. Thus these products are good candidates to prepare some biobased FR compounds. Some studies found in the literature explored this way. Marosi et al. [13] carried out the selective phosphorylation and phosphinylation of hydroquinone and phloroglucinol with diethyl chlorophosphate and diphenylphosphonyl chloride by a nucleophile substitution reaction (SN_2). Ren et al. [14] used the same reaction (SN_2) to carry out the dimerization of catechol functionalizing the hydroxyl groups with the phenyl phosphonic dichloride to form a phosphorus-containing aromatic diphenol which is glycidylated to obtain a reactive phosphorus-containing flame retardant.

The purpose of the present study is to synthesize and evaluate new biobased phosphate flame retardant additives for epoxy thermoset. To promote the charring effect, we have chosen to work with phosphate groups. Our strategy consists in functionalizing a biobased phenolic compound with different dialkyl chlorophosphate groups by a Williamson reaction. The chosen biobased resource for this study is the phloroglucinol thanks to its symmetrical structure, which allows the three hydroxyl functions to show the same reactivity. Different parameters were studied such as the influence of the **R** group present in P-O-**R** phosphonic ester or the thermoset phosphorus content.

The flame retardant properties of the synthesized FR and their impact on thermoset physical properties were assessed in an epoxy matrix commonly used, the diglycidylether of bisphenol A (DGEBA) cross-linked by the isophorone diamine (IPDA).

Experimental part

Reagents

Dimethyl chlorophosphate, diethyl chlorophosphate, diphenyl chlorophosphate, phloroglucinol, and potassium carbonate were purchased from Sigma-Aldrich. Triethyl amine was supplied from Acros organics. For epoxy resins components, diglycidylether of bisphenol A (DGEBA) resin and isophorone diamine (IPDA) as curing agent were purchased from Sigma-Aldrich.

Synthesis

Synthesis of phloroglucinol-tris(dimethyl phosphate): *P3P(OMe)*

Phloroglucinol (5.0 g, 0.040 mol, 1 eq) and potassium carbonate (21.9 g, 0.159 mol, 4 eq) (potassium carbonate was used to limit the water treatment during the purification step) were introduced with 60 mL of acetone in a 100 mL two-necked round-bottomed flask equipped with a stirrer, a rubber septum and a condenser connected to a high purity nitrogen source. The solution was heated at 60 °C under vigorous stirring. Dimethyl chlorophosphate (20.1 g, 0.139 mol, 3.5 eq) was introduced slowly. After 5 h reaction, potassium carbonate was removed by filtration, the filtrate solvent was evaporated and the residue taken up in a mixture of 150 mL of chloroform and 20 mL of water. The organic phase is dried with sodium sulfate and the solvent evaporated to obtain a yellow liquid. Yield: 60 %

P3P(OMe) – $^1\text{H-NMR}$ (400 MHz, δ , ppm): 7.05 [3H, ArCH]; 3.85 [18H, P-OCH₃]; $^{13}\text{C-NMR}$ (400 MHz, δ , ppm): 152.8 [ArC_q]; 109.8 [ArCH]; 55.6 [P-OCH₃]; $^{31}\text{P-NMR}$ (400 MHz, δ , ppm): -4.46.

Synthesis of phloroglucinol-tris(diethyl phosphate): *P3P(OEt)*

Phloroglucinol (5.0 g, 0.040 mol, 1 eq) and triethyl amine (16.0 g, 0.159 mol, 4 eq) were introduced with 60 mL of acetone in a 100 mL two-necked round-bottomed flask equipped with a stirrer, a rubber septum and a condenser connected to a nitrogen source. The solution was heated at 60 °C under vigorous stirring. Diethyl chlorophosphate (24.0 g, 0.139 mol, 3.5 eq) was introduced slowly. After 5 h reaction, the system was filtered, the filtrate solvent was evaporated and the residue taken up in a mixture of 150 mL of chloroform and 50 mL of water. The organic phase was washed with water, dried with sodium sulfate and the solvent evaporated to obtain a brown oil. Yield: 66 %.

P3P(OEt) – $^1\text{H-NMR}$ (400 MHz, δ , ppm): 7.07 [3H, ArCH]; 4.24 [12H, P-OCH₂CH₃]; 1.35 [18H, P-OCH₂CH₃]; $^{13}\text{C-NMR}$ (400 MHz, δ , ppm): 152.9 [ArC_q]; 109.8 [ArCH]; 62.5 [P-OCH₂CH₃]; 16.4 [P-OCH₂CH₃]; $^{31}\text{P-NMR}$ (400 MHz, δ , ppm): -6.73.

Elemental analysis: Calc. %: C: 40.46, H: 6.22, O: 35.93, P: 17.39; Found %: C: 38.19, H: 6.66, O: 35.05, P: 17.10.

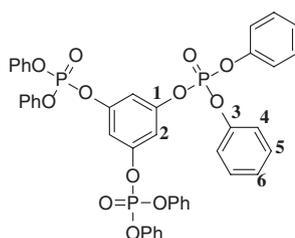
Synthesis of phloroglucinol-tris(diphenyl phosphate): *P3P(OPh)*

Phloroglucinol (5.0 g, 0.040 mol, 1 eq) and triethyl amine (16.0 g, 0.159 mol, 4 eq) were introduced with 80 mL of acetone in a 100 mL two-necked round-bottomed flask equipped with a stirrer, a rubber septum and a condenser connected to a high purity nitrogen source. The solution was heated at 60 °C under vigorous stirring. Diphenyl chlorophosphate (37.3 g, 0.139 mol, 3.5 eq) was introduced slowly. After 5 h reaction, the system is filtered, the filtrate solvent was evaporated and the residue taken up in a mixture of 200 mL of chloroform and 50 mL of water. The organic phase was washed with water, dried with sodium sulfate and the solvent evaporated to obtain a yellow solid. Yield: 74 %.

P3P(OPh) – ¹H-NMR (400 MHz, δ, ppm): 7.41 [12H, C₄-H]; 7.29 [21H, C₂-H, C₅-H and C₆-H];

¹³C-NMR (IG) (400 MHz, δ, ppm): 152.4 [3C, C₁]; 151.1 [6C, C₃]; 130.9 [12C, C₄];

126.8 [6C, C₆]; 120.9 [12C, C₅]; 110.9 [3C, C₂]; ³¹P-NMR (400 MHz, δ, ppm): -17.98.



Elemental analysis: Calc. %: C: 61.32, H: 4.04, O: 23.34, P: 11.30; Found %: C: 60.54, H: 3.95, O: 23.07, P: 10.96.

Thermosets preparation

Different thermosets were prepared with the different FRs synthesized to evaluate the influence of phosphorus content and the nature of the phosphate groups on the flame retardancy. Table 1 summarizes data for thermosets preparation.

The FR was solubilized in DGEBA under stirring at 80 °C for 10 min. The mixture was cooled at 50 °C to avoid any crosslinking upon mixing with the hardener. A stoichiometric epoxy/amine ratio (2/1) was used. The system was stirred manually for 5 min. Lastly the mixture was crosslinked in a circular rubber mold

Table 1 Compositions of the formulated epoxy thermosets.

Thermosets	Weight composition (% _w) (DGEBA/IPDA/FR)	Used FR	Phosphorus content (% _w P/thermoset)
Reference	(80/20/0)	None	0
1 %P(<i>P3P(OMe)</i>)	(76.0/19.0/5.0)	<i>P3P(OMe)</i>	1
2 %P(<i>P3P(OMe)</i>)	(72.1/18.0/9.9)	<i>P3P(OMe)</i>	2
3 %P(<i>P3P(OMe)</i>)	(68.1/17.00/14.9)	<i>P3P(OMe)</i>	3
4 %P(<i>P3P(OMe)</i>)	(64.2/16.1/19.7)	<i>P3P(OMe)</i>	4
1 %P(<i>P3P(OEt)</i>)	(75.4/18.9/5.7)	<i>P3P(OEt)</i>	1
2 %P(<i>P3P(OEt)</i>)	(70.8/17.7/11.5)	<i>P3P(OEt)</i>	2
3 %P(<i>P3P(OEt)</i>)	(66.2/16.6/17.2)	<i>P3P(OEt)</i>	3
4 %P(<i>P3P(OEt)</i>)	(61.6/15.4/23.0)	<i>P3P(OEt)</i>	4
1 %P(<i>P3P(OPh)</i>)	(73.0/18.2/8.8)	<i>P3P(OPh)</i>	1
2 %P(<i>P3P(OPh)</i>)	(65.9/16.4/17.7)	<i>P3P(OPh)</i>	2
3 %P(<i>P3P(OPh)</i>)	(58.8/14.7/26.5)	<i>P3P(OPh)</i>	3
4 %P(<i>P3P(OPh)</i>)	(51.7/12.9/35.4)	<i>P3P(OPh)</i>	4

The bold values represent the weight % of phosphorus contained in the epoxy resin.

according to the following temperature program: 4 h at 80 °C and 10 h at 150 °C. Thermosets were named according to their phosphorus content followed by the used FR: “x%P(used FR)”. The reference thermoset was the stoichiometric system DGEBA/IPDA (2/1).

Characterizations

Chemical structures of the prepared compounds were determined by ^{31}P -NMR, ^{13}C -NMR (IG) and ^1H -NMR spectroscopy in a Bruker Avance 400 MHz spectrometer at room temperature in $(\text{CD}_3)_2\text{CO}$ solutions. External references were trimethylsilane (TMS) for ^1H -NMR and ^{13}C -NMR and phosphoric acid (H_3PO_4) for ^{31}P -NMR. Shifts are given in ppm.

Chemical structures of *P3P(OEt)* and *P3P(OPh)* were confirmed by elemental analyses.

- Thermal analyses were performed using samples grounded with cryogenic grinder SPEX6770.
- Thermogravimetric analyses were performed using a Pyris 1 TGA Perkin Elmer at a heating rate of 10 °C/min under nitrogen atmosphere.
- Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-Octadecane and n-Octane standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at 10 °C/min between 20 and 200 °C to observe the glass transition temperature determined as the inflexion value in the heat capacity jump and the residual curing.

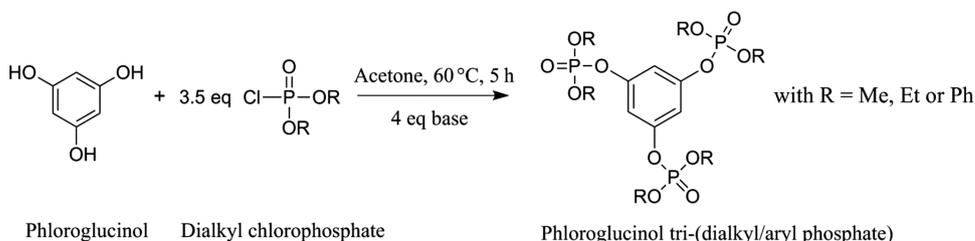
Samples were observed using a FEI Quanta 200 scanning electron microscope and phosphorus content was determined by energy dispersive X-ray spectroscopy (EDX) using Oxford INCA Energy 300 system and a detector of 133 eV (at Mn). Samples were characterized after metallization in high vacuum sputtering metallizer Bal-Tec CED 030 Blatzer.

Flammability was assessed using a pyrolysis-combustion flow calorimeter from Fire Testing Technology (FTT UK). About 3 mg was placed in the pyrolyzer, undergoing an increase of temperature from 20 °C to 750 °C at 1 °C/s under a nitrogen flow. Decomposition gases were sent to a combustor heated at 900 °C under air flow ($\text{N}_2/\text{O}_2 = 80/20$). At this temperature and with 20 % of oxygen, combustion was considered to be complete. Heat release rate was determined by oxygen depletion according to Huggett principle [15] (1 kg of consumed oxygen corresponds to 13.1 MJ of heat released).

Results and discussion

Synthesis of phloroglucinol tris-[di-alkyl/aryl(R) phosphate] compounds

Williamson etherification [16] is a well-known organic reaction regarding the O-alkylation of an alcohol with halide, leading to an ether bond. This reaction was performed between chlorophosphate and biobased phloroglucinol and showed a similar reactivity of the three hydroxyl functions. The use of a chlorophosphate and phloroglucinol allows the formation of phosphonic ester functions between the aromatic ring and the phosphorus atom. The synthesis of phloroglucinol tris-(di-R phosphate) was carried out by using a phloroglucinol/chlorophosphate ratio of 1.0/3.5 (Scheme 1). The formation of the phenolate ion is usually carried out by the introduction of a conventional base but can also be performed by the presence of metal as zinc [17]. Triethylamine was chosen for the syntheses using diethyl-chlorophosphate and diphenyl-chlorophosphate to obtain phloroglucinol-tris(diethyl phosphate) (P3P(OEt)) and phloroglucinol-tris(diphenyl phosphate) (P3P(OPh)), respectively. K_2CO_3 was used as the base for the P3P(OMe) synthesis. The conversion of hydroxyl functions was complete for any R groups and the average yield of these three syntheses was around 70 %.



Scheme 1 Synthesis of FR by nucleophilic substitution of chlorophosphate onto phloroglucinol.

NMR characterizations

Phosphate functionalities of P3P(OMe) and P3P(OEt) were determined by ^1H -NMR (SI.1.) and the degree of purity was assessed by ^{13}C -NMR (SI.2.). Results show a total conversion of hydroxyl groups and pure products after purification. However, for the compound P3P(OPh) the signals of all the aromatic protons overlapped; hence, the ^1H -NMR spectroscopy does not allow determining the phosphate functionality. Quantitative ^{13}C -NMR spectra can be obtained by inverse gated (IG) decoupling and long accumulating delays of 60 s between two pulses. Thus, quantitative ^{13}C (IG)-NMR was used and showed a total conversion of hydroxyl groups into phosphate groups (Fig. 1).

These three FR P3P(OMe), P3P(OEt) and P3P(OPh) possess different phosphorus contents, 20.7 wt%, 17.4 wt% and 11.3 wt%, respectively. The FR contents incorporated into the epoxy resin were adjusted to range the phosphorus content in the thermoset from 1 to 4 wt%P/thermoset.

Thermal stability of the FRs

Figure 2 represents TGA thermograms performed for all FR. Concerning the thermal stability of the three FR, it shows that the main thermal degradation step starts beyond 150 °C for all FR. However, it is observed that the thermal behaviors for the three FR are rather different. R groups used on phosphate impacts the dissociation energy of the P-O bond. The P3P(OMe) and P3P(OEt) FRs, which bear an alkyl group bonded to their phosphate group show similar thermal stabilities; their T_{10} (T_{10} represents the temperature at which the thermoset loses 10 % of its initial mass) are 228 and 198 °C, respectively. However, P3P(OPh) FR, which has an aryl group bonded to the phosphate group, displays a better thermal stability. Indeed, its T_{10} value is 364 °C. P3P(OPh) FR which exhibits only one type of P-O bonds decomposes in a single step beyond 400 °C, while the P3P(OEt) and P3P(OMe) FR which have two types of P-O bond, decompose in two steps: the first one is around 250 °C

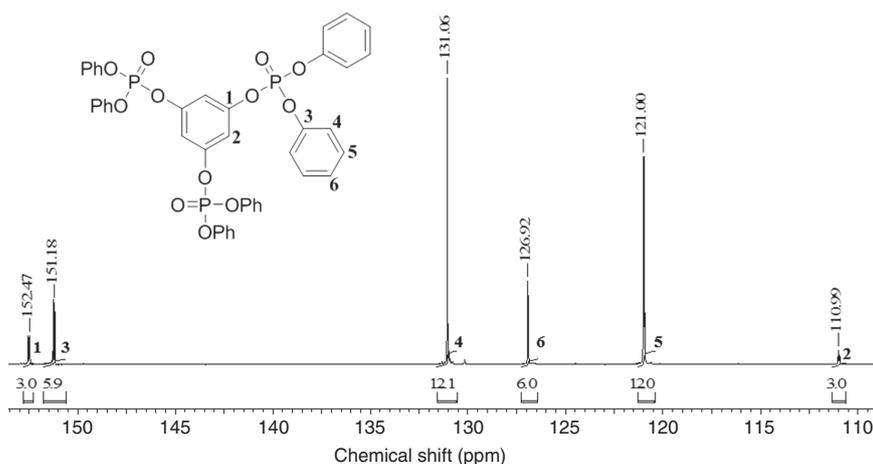


Fig. 1 Quantitative ^{13}C (IG)-NMR spectrum of P3P(OPh).

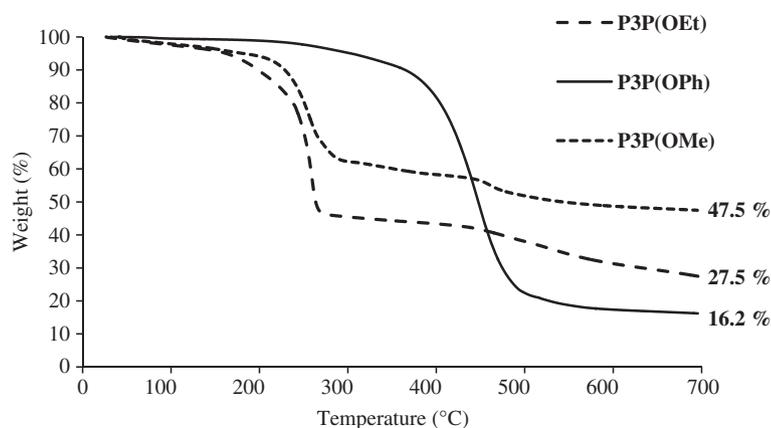


Fig. 2 TGA thermograms of the synthesized flame retardants P3P(OMe), P3P(OEt) and P3P(OPh) under nitrogen atmosphere at 10 °C/min.

and corresponds to the P-O bond scission followed by the formation of phosphonic anhydride [18]; while, the second one around 450 °C corresponds to the reorganization of the formed anhydride. This difference can be explained by the mesomeric donor effect of the aromatic ring which stabilizes the P-O bond until higher temperature and allows the two mechanisms to occur at the same temperature. The char amounts at 700 °C are also different: the P3P(OMe), P3P(OEt), P3P(OPh), which contain 20.7 wt%P, 17.5 wt%P and 11.3 wt%P, respectively, undergo 47.5 wt%, 27.0 wt% and 16.2 wt% of char. Thus the higher the phosphorus content of the FR, the higher the intrinsic char amount at 700 °C. An apparent charring efficiency which correspond to the char content reported to the initial phosphorus content can also be determined: 2.29 for P3P(OMe), 1.54 for P3P(OEt) and 1.43 for P3P(OPh). Among them, P3P(OMe) presents the highest charring efficiency.

Formulations and characterizations of flame retarded resins

Incorporation in epoxy matrix and assessment of the compatibility FR/matrix

To evaluate their efficiency as FRs, phosphorus based additives were introduced in a conventional epoxy matrix, i.e., DGEBA, cured by IPDA (Fig. 3). The DGEBA exhibits an aromatic structure leading to rigid network with excellent mechanical properties and good chemical inertness. That is why DGEBA is widely used, especially in the production of coatings or high performance composites [19, 20]. Isophorone diamine is a cycloaliphatic cross-linking agent and appears to provide a good balance between reactivity and network rigidity. The matrix was also chosen according to FR degradation temperature, which has to be higher than the curing temperature to avoid FR degradation during the thermoset cross-linking.

Epoxy/amine ratio was fixed to 2/1 in order to optimize the cross-linking. The reaction between an epoxy function and a primary amine forms a secondary amine which is then able to react with another epoxy function [21]. Indeed, thermal stability of thermosets is directly dependent on the cross-linking density.

The curing conditions of this matrix were determined in our previous study [7]. Different thermosets were prepared with various FR and phosphorus contents. Thermosets were named according to their phosphorus content followed by the used FR: “x%P(used FR)”.

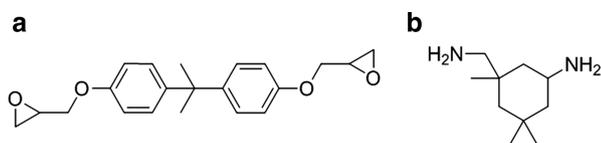


Fig. 3 (a) Diglycidylether bisphenol A (DGEBA), (b) isophorone diamine (IPDA).

A possible incompatibility between the matrix and the FR could lead to a partial phase segregation. During early stages of curing, viscosity of the system decreases and may allow sedimentation or creaming of segregated phases. The homogeneity of the cured thermosets was studied by scanning electron microscopy with EDX.

Figure 4 represents pictures and SEM pictures ($\times 2000$) of 3 %P(P3P(OMe)), 3 %P(P3P(OEt)), 3 %P(P3P(OPh))-thermosets. SEM picture of 3 %P(P3P(OMe)) shows the presence of different phases (Fig. 4, 1-b) at the micrometric scale. This phase segregation visually results in an opaque material (Fig. 4, 1-a). The thermosets prepared with P3P(OEt) and P3P(OPh) are translucent (Fig. 4, 2-a, 3-a) and their SEM pictures show the presence of a single phase. These results evidence a better compatibility between the FR and the matrix for the P3P(OEt) and P3P(OPh) compounds compared to P3P(OMe).

Phosphorus content was determined at different depths from the upper to the lower surface of 3 %P(P3P(OMe)) and 3 %P(P3P(OEt)) (Fig. 5). The 3 %P(P3P(OEt))-thermoset shows a homogeneous distribution of the phosphorus content; such as 3 %P(P3P(OPh))-thermoset, whereas a significant evolution of phosphorus content is observed for the 3 %P(P3P(OMe))-thermoset. These results evidence that the biphasic structure observed in Fig. 4 allows the sedimentation of the phosphorus phases and leads to a gradient in phosphorus content of thermosets. The biphasic structure of the P3P(OMe)-containing thermoset have to be taken into account regarding the flame retardant properties of these thermosets.

DSC analyses of cross-linked thermosets

Physical properties of thermosets can be assessed measuring their glass transition temperature (T_g). The T_g is the temperature needed to break the non-covalent inter-chains interactions. It corresponds to the relaxation of the network and the transition between the brittle and the rubbery states. Most often, high T_g are targeted for the thermosets to reach both high thermal and mechanical properties.

DSC analyses were performed on cross-linked thermosets. Figure 6 shows the evolution of the T_g values when increasing the phosphorus content for each thermoset. Two distinct behaviors are clearly observed. When both P3P(OEt) and P3P(OPh) are used as additives in the epoxy matrix, a decrease of the T_g values with the phosphorus content is noted. Since these FR additives are homogeneously distributed into the matrix, they then act as plasticizers and create space between network chains, thus reducing the crosslinking density.

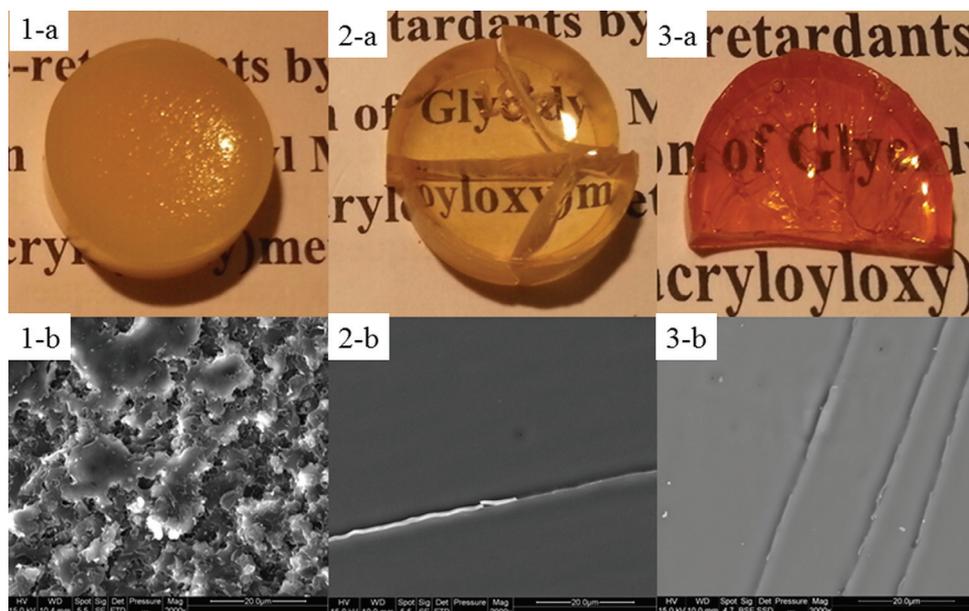


Fig. 4 Pictures (a) and SEM pictures $\times 2000$ (b) of thermosets 3 %P(P3P(OMe)) (1), 3 %P(P3P(OEt)) (2), 3 %P(P3P(OPh)) (3).

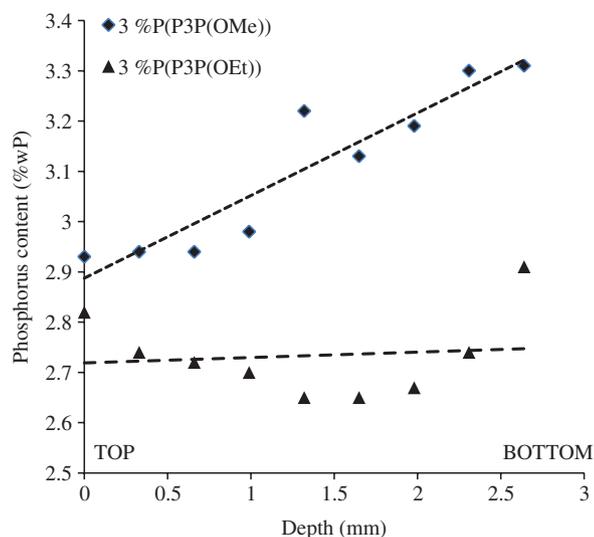


Fig. 5 Evolution of the phosphorus content vs. the depth from the surface in the 3 %P(P3P(OMe)) and 3 %P(P3P(OEt)) thermosets.

For similar phosphorus content, T_g values determined for the P3P(OPh)- and P3P(OEt)-containing thermosets are comparable even both FRs are incorporated in different amounts into the thermosets. On the one hand, the plasticizing effect of the P3P(OPh) should be more significant due to the larger FR size but on the other hand, this effect is counterbalanced by a higher rigidity induced by the FR aromaticity. The second behavior is observed when P3P(OMe) is used as additive. T_g values determined for these thermosets do not follow the same trend than as that of all other thermosets. Indeed, for the same phosphorus content, i.e., 1%_w, T_g values are 126 °C and 150 °C for P3P(OMe) and P3P(OEt), respectively.

The P3P(OMe) FR introduced in small amount in the material plasticized the network due to the formation a segregated microphase which avoids the intramolecular interactions between the chains. However, when P3P(OMe) was introduced in higher amounts, T_g values were less affected and almost comparable to that of the reference one. Indeed, 3 %P(P3P(OMe)) and 4 %P(P3P(OMe)) thermosets show T_g values of 140 and 153 °C, respectively. The increase of the phosphorus content for P3P(OMe)-containing thermosets generates strong phase segregation and the FR does not act as plasticizer anymore.

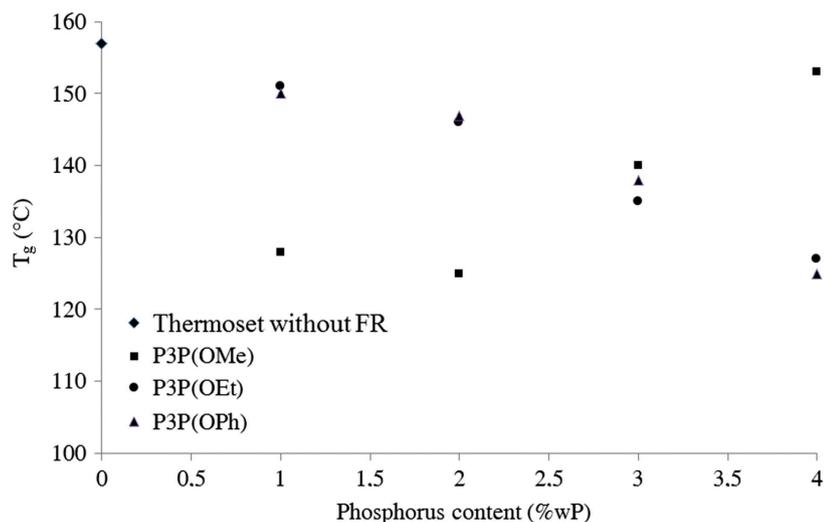


Fig. 6 T_g values obtained by DSC analyses vs. the phosphorus content in all thermosets.

Thermal properties and flammability of epoxy thermosets

Phosphorus-containing FRs are known for their different flame-retardancy mechanisms. They can act in gas and/or in condensed phases [22]. In the gas phase, they act by flame inhibition. Thermal decomposition of phosphorus group can generate radical species $\text{PO}_2\cdot$, $\text{PO}\cdot$ and $\text{HPO}\cdot$, which scavenge the $\text{H}\cdot$ and $\text{OH}\cdot$ radicals, slowing down the combustion and even reducing the combustion efficiency. In the condensed phase, chains dehydroxylation occur due to the action of phosphoric acid onto the hydroxyl groups, leading to conjugated molecules, and then to polyaromatic structures by Diels-Alder cyclization [4]. The formed char can act as a barrier against heat and gas (O_2 and pyrolysis gases).

The flammability of the different thermosets was assessed according to different parameters such as high temperature char amounts, heat release rates or total heat released during decomposition. Thermosets are characterized by thermogravimetric and pyrolysis combustion flow calorimetry (PCFC) analyses to highlight the effects of FR on the thermal properties and flammability.

Thermogravimetric analyses of flame retarded thermosets

TGA analyses were performed to assess the influence of FR on thermal stability and charring of the flame retarded thermosets. T_{10} represents the temperature at which the material loses 10 % of its initial mass. Figure 7 compares the thermoset without FR to the three thermosets, each containing 3 %_wP. Thermosets 3 %_wP(P3P(OMe)), 3 %_wP(P3P(OEt)), 3 %_wP(P3P(OPh)) exhibit lower thermal stabilities than that of the thermoset without FR. Indeed their T_{10} are respectively 311, 307 and 304 °C compared to 369 °C for the thermoset without FR. These lower degradation temperatures are assigned to the early stage of decomposition for phosphorus-containing groups. Price et al. [23] described the phosphonic-ester decomposition ranging between 300 and 340 °C by alkyl chain loss. It may be assumed that phosphonic-ester decomposition generates radical species which initiate the matrix decomposition.

For a phosphorus content of 3 %_w, the three thermosets 3 %_wP(P3P(OMe)), 3 %_wP(P3P(OEt)) and 3 %_wP(P3P(OPh)) contains FR in different amounts, 14.9 %_w of P3P(OMe), 17.2 %_w of P3P(OEt) and 26.5 %_w

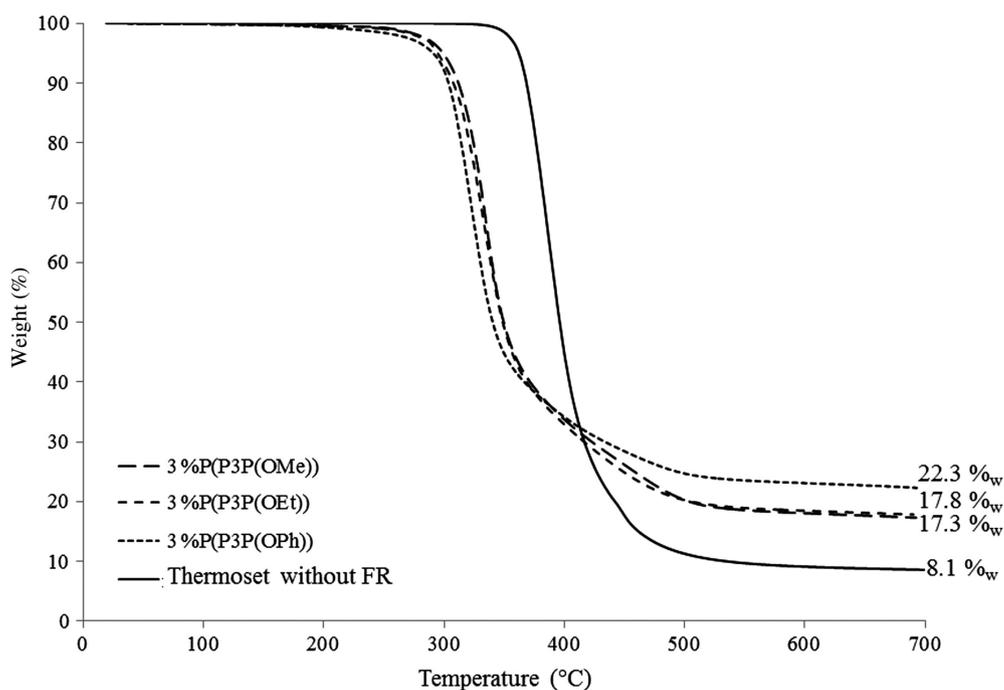


Fig. 7 TGA thermograms of 3 %_wP-containing thermosets compared to the thermoset without FR.

of P3P(OPh), respectively. However these three thermosets displayed similar thermal stability, i.e., their T_{10} are in the 304–311 °C range. This result was verified on other phosphorus content and thus shows that the thermal stability of thermoset is only modified by the phosphorus content, not by nature of the phosphate group. The influence of the phosphorus content on the thermal behavior of the thermoset is also studied. TGA thermograms of thermosets *reference* and P3P(OPh)-containing thermosets are presented in Fig. 8 and show that the higher the phosphorus content of a thermoset, the lower its thermal stability. Thus, thermal stability of the thermosets is impacted by the phosphorus content.

Figure 7 also exhibits that phosphorus-containing thermosets provide a higher amount of stable residue at high temperature than the thermoset without FR. The 3 %_wP(P3P(OMe)) and 3 %_wP(P3P(OEt))-thermosets provide equivalent char amount between 17 and 18 %_w. The thermoset 3 %_wP(P3P(OPh)) generates about 22.3 %_w of char, i.e., three times higher than that of the thermoset without any FR.

Expected char contents have been calculated with an addition law by summing the respective char content of each component of the system. These calculated char content do not consider the action of the FR on the matrix. Results are given in Table 2. It is observed that experimental values are higher than the theoretical ones. It demonstrates the action of the three FR additives to promote charring of the matrix. However, even if P3P(OMe) displays the intrinsically higher charring efficiency, when the three FR are introduced into the matrix, P3P(OPh) allows a better charring effect on the matrix. TGA curves of the P3P(OPh)-containing thermosets (Fig. 8) also exhibit an increase in the char content when phosphorus rate increases. With 4 %_wP brought by P3P(OPh), the epoxy thermoset generates more than three times the char amount obtained with the thermoset without any FR. It shows the ability of this aromatic biobased polyphosphate to improve the charring effect of an epoxy matrix during its thermal degradation. The same trend was observed on TGA thermograms of P3P(OEt)-containing thermosets. TGA thermograms of P3P(OMe)-containing thermosets are not

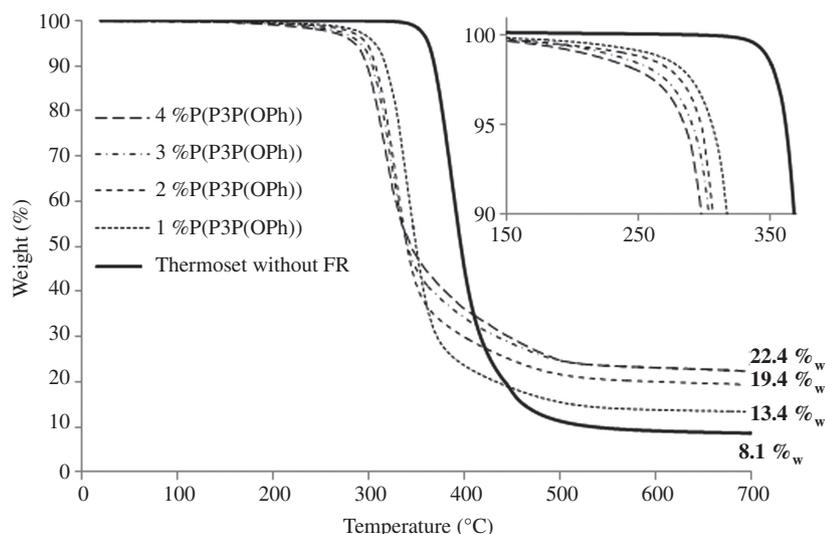


Fig. 8 TGA thermograms of P3P(OPh)-containing thermosets compared to the thermoset without FR.

Table 2 Comparisons between calculated and experimental char content values for 3 %P(P3P(OMe)), 3 %P(P3P(OEt)) and 3 %P(P3P(OPh)) thermosets.

Thermosets	Calculated char content ^a (% _w)	Experimental char content ^b (% _w)	$\Delta(\text{exp-calc})$
3 %P(P3P(OMe))	14.0	17.3	3.3
3 %P(P3P(OEt))	11.4	17.8	6.4
3 %P(P3P(OPh))	10.2	22.3	12.1

^a%Char calculated = (%FR/thermoset) x (%char FR) + (%matrix/thermoset) x (%char matrix).

^bForm TGA.

presented in this study because of some reproducibility issue probably due to the heterogeneous structure as discussed above.

Flammability analyses: pyrolysis combustion flow calorimetry (PCFC)

To assess the flame retardant properties of synthesized phosphate, thermosets were characterized by pyrolysis/combustion flow calorimetry. PCFC analyses correspond to anaerobic thermoset pyrolysis followed by the high temperature oxidation of decomposition products (complete combustion) [24].

pHRR is the maximal value of the heat release rate. T_{α} represents the temperature at pHRR. The total heat released (THR) was obtained by integration of PCFC curves. The effective heat of combustion (EHC) represents the released heat by lost mass. It is calculated as the ratio between THR/mass loss measured in TGA.

The reference values for pHRR and THR were respectively 664 W/g and 34.2 kJ/g. For equal phosphorus contents, HRR curves of the thermoset containing P3P(OMe), P3P(OEt) and P3P(OPh) exhibit equivalent HRR curves (Fig. 9).

Figure 10 also shows the similar action of the three phosphates FR on the different parameters studied (pHRR, THR, T_{α} and EHC). Peak of heat release rate (Fig. 10a) is significantly reduced, from 664 W/g for the thermoset without FR to around 400 W/g for the thermosets containing 3 %_wP brought by any of the phosphate FR, i.e., a decrease of 40 %.

The total heat released is also reduced (Fig. 10b) from 34 kJ/g for the thermoset without FR to around 27 kJ/g for the thermosets containing 3 %_wP brought by any of the phosphate FR, i.e., a decrease of 21 %. The THR decreased linearly by increasing the phosphorus content, which increases the char content at high temperature. Indeed, the charring reduces the amount of decomposition gases which are able to participate to the combustion and thus reduces the total heat released by the thermoset. Nevertheless, the THR appears to be slightly higher with P3P(OPh) than with other FR, at least at high phosphorus content, despite the higher char amount of this thermoset.

Combining the char rate obtained by TGA to the THR measured by PCFC analyses allows determining the EHC for P3P(OEt) and P3P(OPh)-containing thermosets. Figure 10d shows a decrease of the EHC values starting from 2 to 3 %_wP. If phosphorus content is lower than this value, EHC remains constant and highlights the action of the FR in the condensed phase. The T_{α} of the thermoset (Fig. 10c) is also reduced by the phosphorus amount. From 385 °C for the reference thermoset to around 330 °C for the thermosets containing 4 %_wP. This loss of thermal stability is comparable to that observed from TGA analyses (Fig. 7).

However, for similar phosphorus contents, the different FR were not introduced into the same amount in the resin formulation. Thus, the similar behavior of the thermosets containing the same phosphorus content brought by the different FRs shows that the additive content and its nature do not affect the flammability of the thermoset. Moreover, the structural heterogeneity observed for P3P(OMe)-containing thermosets does not

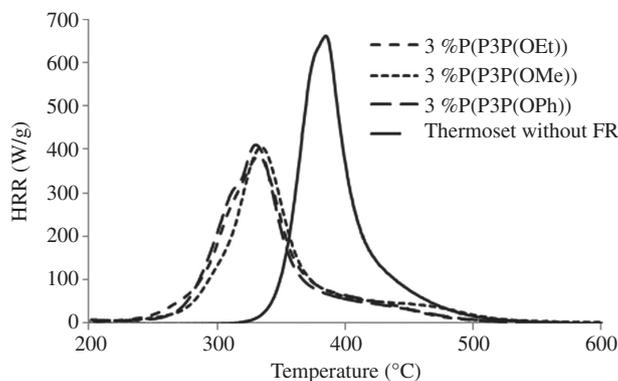


Fig. 9 PCFC curves of the 3 %_wP-containing thermosets compared to the thermoset without FR.

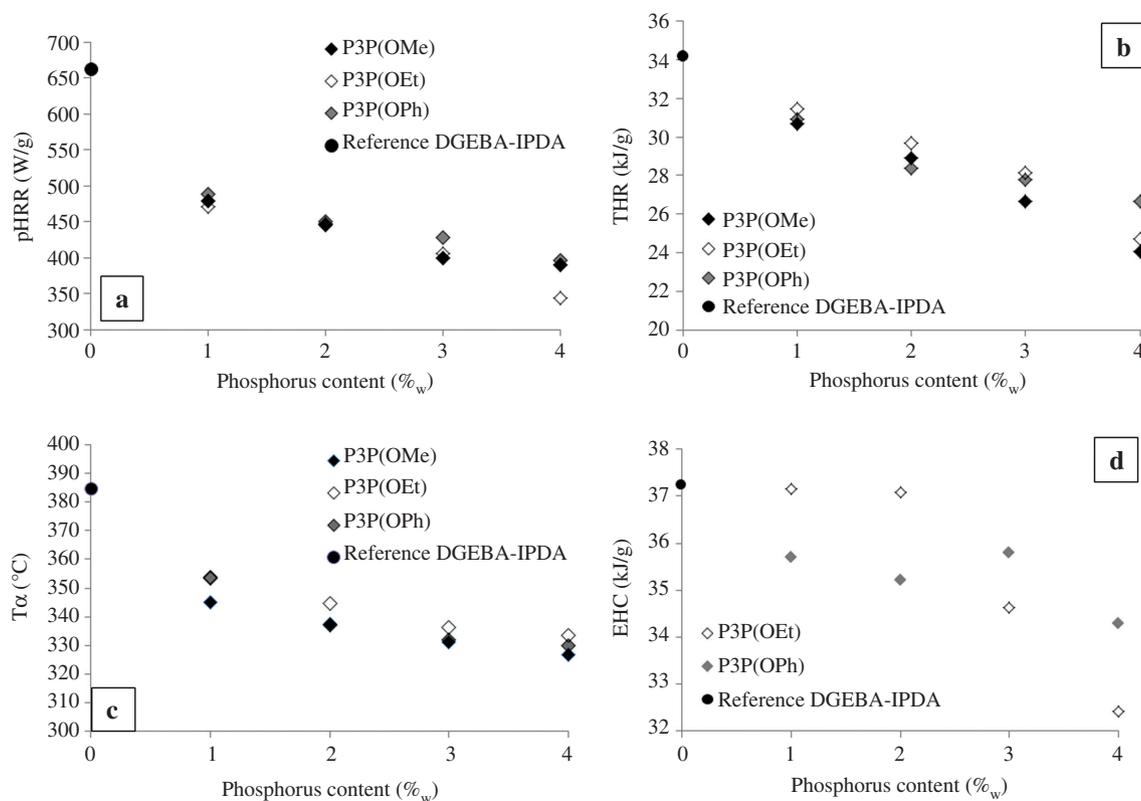


Fig. 10 Evolution of pHRR (a), THR (b), T_α (c) and EHC (d) vs. initial phosphorus content of all thermosets.

influence the action of the FR. This result could show that a micrometric repartition of the FR in the matrix is enough to ensure good FR properties. Nevertheless, it could also be assumed that a high temperature would better homogenize the RF into the thermoset. However, the incompatibility observed between the P3P(OMe) FR and the DGEBA-IPDA matrix has probably an influence on the migration of the FR in the cross-linked thermoset and favors a non permanent thermal behavior. In this study, the flammability of thermosets was studied just after manufacturing, not after ageing. Thus, it is observed that only the initial phosphorus content has an influence on the flammability of the thermosets.

Conclusion

Williamson etherification was successfully used on phloroglucinol to synthesize some phosphorus-containing biobased phosphates with different R groups in the phosphate groups P-O-R. The average yield of these synthesis is around 70 %. Flame retardant properties of these phosphates were evaluated in an epoxy matrix. The influence of R group of the phosphate P-O-R was evidenced by obtaining opaque thermosets which display phase heterogeneity using a methoxy phosphate. It showed the importance of the compatibility between FR and matrix structures to preserve visual aspect of the thermoset and to obtain homogeneous thermosets. A plasticizing effect was highlighted by the decrease of the glass transition temperatures of thermosets by introducing any of the FR. TGA and PCFC analyses showed that thermosets flammability mainly depends on the phosphorus content. A decrease in the thermal stability was observed for all phosphorus-containing thermosets, and is attributed to the earlier decomposition of phosphorus groups. Nevertheless, this decrease in thermal stability is accompanied by a significant increase in char yield and reduction of flammability. Indeed, THR was reduced by 21 % and pHRR by 40 % with 3 wt%P compared to the that of thermoset without FR. The heterogeneity of the P3P(OMe)-containing thermosets does not influence the action of the FR

on the matrix. However, this heterogeneity should promote the migration of the additive into the network and hence modify its FR efficiency. The chosen biobased resource is a model molecule of the biophenol really targeted. So far, the phloroglucinol is produced by bacterial fermentation of glucose and has a limited availability. However, some biobased phenolic compounds such as gallic acid are more available than the phloroglucinol and could be used from the same synthesis pathway for a possible development as new biobased FR.

References

- [1] E. N. Walsh, E. J. Griffith, R. W. Parry, L. D. Quin. *ACS Symposium Series 468: Phosphorus Chemistry*. Development in American Science, ACS, Washington, DC; pp. XIII, XXIX, 218 (1992).
- [2] REACH, *Commission of regulation (EC) No 552/2009, Official Journal of the European Union, L 164/17*.
- [3] RoHS, *Directive 2002/95/EC of the european parliament and of the council, Official Journal of the European Union, L 37/19*.
- [4] S. Y. Lu, I. Hamerton. *Prog. Polym. Sci.* **27**, 1661 (2002).
- [5] U. Braun, A. I. Balabanovich, B. Schartel, U. Knoll, J. Artner, M. Ciesielski, M. Döring, R. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech. *Polymer* **47**, 8495 (2006).
- [6] P. M. Hergenrother, C. M. Thompson, J. G. Smith Jr, J. W. Connell, J. A. Hinkley, R. E. Lyon, R. Moulton. *Polymer* **46**, 5012 (2005).
- [7] R. Ménard, C. Negrell-Guirao, L. Ferry, R. Sonnier, G. David. *Eur. Polym. J.* **57**, 109 (2014).
- [8] D. Kyriacos. *Fire-retardants for polymers*, edited by *GEM-Chem*; ISBN: 9789078546269 (2012).
- [9] Z. Zheng, B. W. T. Y. S. Liu, X. Cui, H. Wang. *Polym. Composite*. n/a-n/a (2014).
- [10] S. Ma, X. Liu, Y. Jiang, L. Fan, J. Feng, J. Zhu. *Sci. China Chem.* **57**, 379 (2014).
- [11] G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz. *J. Polym. Sci. Part A: Polym. Chem.* **44**, 6717 (2006).
- [12] T. Sowa, S. Ouchi. *Bull. Chem. Soc. Jpn* **48**, 2084 (1975).
- [13] G. Marosi, A. Toldy, G. Parlagh, Z. Nagy, K. Ludányi, P. Anna, G. Keglevich. *Heteroatom Chem.* **13**, 126 (2002).
- [14] H. Ren, J. Sun. B. Wu, Q. Zhou. *Polym. Degrad. Stabil.* **92**, 956 (2007).
- [15] C. Huggett. *Fire Mater.* **4**, 61 (1980).
- [16] A. W. Williamson. *Q. J. Chem. Soc. London* **4**, 229 (1852).
- [17] S. Paul, M. Gupta. *Tetrahedron Lett.* **45**, 8825 (2004).
- [18] G. A. Wang, W. M. Cheng, Y. L. Tu, C. C. Wang, C. Y. Chen. *Polym. Degrad. Stabil.* **91**, 3344 (2006).
- [19] L. F. Gonzales, F. Ferrando, X. Ramis, J. M. Salla, A. Mantecon, A. Serra. *Prog. Org. Coat.* **65**, 175 (2009).
- [20] M. Bertocini, J. C. Hoepfner, S. H. Pezzin. *Curr. Org. Chem.* **17**, 1838 (2013).
- [21] R. Auvergne, S. Caillol, G. David, B. Boutevin, J. P. Pascault. *Chem. Rev.* **114**, 1082 (2014).
- [22] S. V. Levchik, E. D. Weil. *Polym. Int.* **54**, 11 (2005).
- [23] D. Price, L. K. Cunliffe, K. J. Bullett, T. R. Hull, G. J. Milnes, J. R. Ebdon, B. J. Hunt, P. Joseph. *Polym. Degrad. Stabil.* **92**, 1101 (2007).
- [24] F. Laoutid, L. Bonnaud. M. Alexandre, J. M. Lopez-Cuesta, P. Dubois. *Mater. Sci. Eng.: R: Reports* **63**, 100 (2009).