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Maxinne Denis, Damien Le Borgne, Rodolphe Sonnier, Sylvain Caillol, Claire Negrell. Flame-retardant performance of phosphorylated furan-containing alkyd resins. *Green materials*, 2024, 12 (3), pp.168-182. 10.1680/jgrma.22.00093 . hal-04143482

HAL Id: hal-04143482

<https://imt-mines-ales.hal.science/hal-04143482v1>

Submitted on 27 Jun 2023

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Improvement of the flame retardant properties of alkyd resins through incorporation of phosphorous-containing furan derivative

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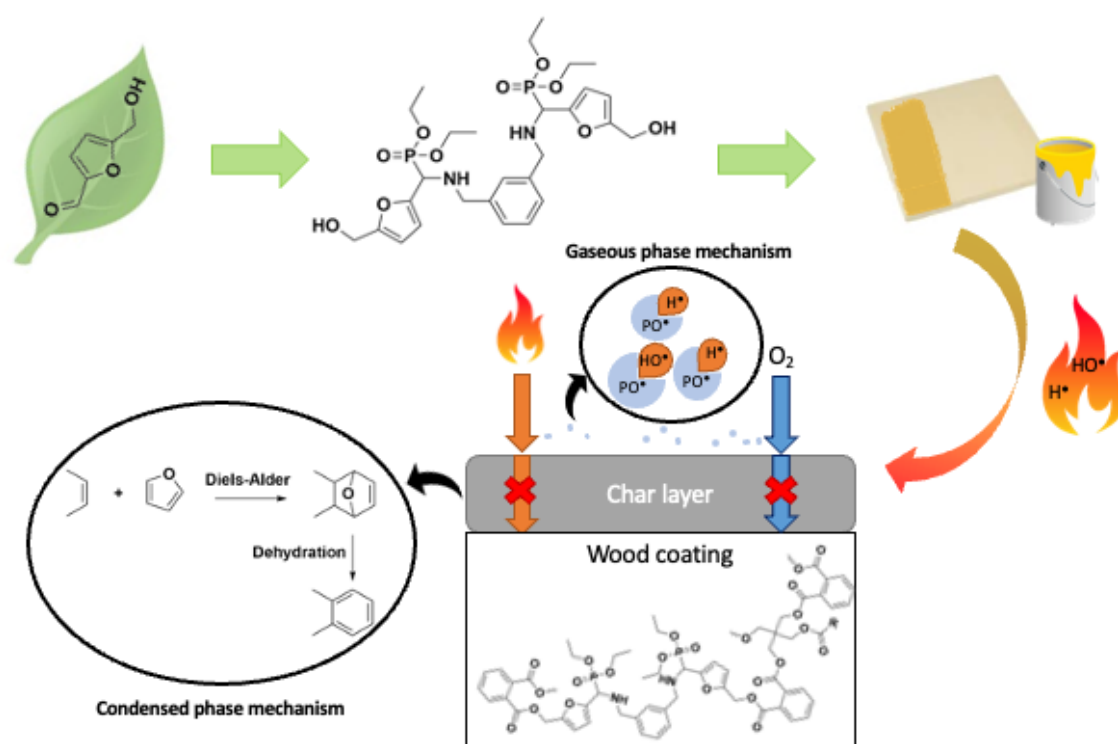
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Graphical abstract



Abstract

Over the past decade, with the emergence of environmental and human health concerns, research has focused on developing new solutions to replace fossil resources with more sustainable biobased resources. Furan derivatives can be obtained from plants and their structures provide high resistance to high temperatures. Therefore, these furan derivatives have been functionalized with phosphorus to increase their fire resistance properties. Thus, a new biobased bisfuran containing nitrogen and phosphorus (HMF-MXDA-DEP) was synthesized and used for the first time in polymerization to develop alkyd resins. The flame retardant properties of these resins have been studied. These alkyd resins are generally used as a binder in paint or varnish formulations. The use of a reactive flame retardant during the polycondensation reaction of alkyd resins makes it possible to form covalent bonds and offer better durability over time. The impact of HMF-MXDA-DEP on film properties such as drying time, flexibility, adhesion and color was studied and the thermal and flame retardant properties by differential scanning calorimeter, thermogravimetric analysis and calorimeter pyrolysis-combustion fluxes were evaluated. Increased thermal stability and good flame retardant (FR)

properties of alkyd resins have been demonstrated. In the cone calorimeter test, the lowest peak in heat release rate (pHRR) was obtained with a 2 wt % coating of P HMF-MXDA-DEP on wood and a 49 % decrease in pHRR compared to FR-free alkyd resins has been demonstrated.

Keywords

Biobased polymers; furan; flame retardant; alkyd resins; phosphonate; coatings

1. Introduction

A major limitation of organic polymers is their flammability due to their structure of carbon and hydrogen which are combustible compounds. For some applications, in particular paints or varnishes for building construction, polymers must be flame retardant. Alkyd resins are used as binders in paint formulation.¹⁻⁴ Flame retardant (FR) properties are generally imparted to paints by a simple introduction of additives such as melamine, ammonium polyphosphate (APP) or other inorganic additives (usually metal oxides or hydrates).⁵⁻⁸

Despite the simplicity of this process, it suffers from several drawbacks such as modifications of the mechanical and physical properties of coatings due to the presence of these solid additives. Therefore, because these FRs are not covalently bonded to the polymer they can migrate, over time, to the surface of the polymer, resulting in a decrease in flammability resistance.⁹ Moreover, these FRs can be released into the environment causing ecological and human health problems.¹⁰ Hence, the introduction of a reactive FR is a good way to overcome these limitations because it allows the formation of covalent bonds between the polymer matrix and the FR.

In recent decades, many reactive halogen compounds have been used to promote the flame retardant properties of alkyd resins, as they exhibit high efficiency at low levels of incorporation.^{9,11-14} Nevertheless, the use of reactive halogen compounds is not an interesting solution because upon combustion they release highly toxic, corrosive and potentially carcinogenic degradation products.^{15,16} Thus, reactive phosphorus-based FRs are the most promising additives to protect alkyd resins from combustion. To be grafted onto alkyd resins, phosphorus-containing FRs must have reactive functions such as carboxylic acid or hydroxyl groups in order to be copolymerized during the step growth polymerization reaction between fatty acids, vegetable oils, polyols and polyacids. Research focuses on the synthesis of novel polyol or polyacid structures containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) as reactive flame retardant in unsaturated polymers, such as phenolic resins or polyesters.¹⁷⁻¹⁹ For this last polymer family, Zhang *et al.* have reported the synthesis of reactive phosphorus based-FR, 2-[10-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-10-yl)]-maleic acid (DOPO-MA) polymerized with polyol and anhydrides.¹⁸ The same authors also have studied flame retardant properties conferred by itaconic acid functionalized with DOPO and copolymerized in polyesters.¹⁷ Additionally, a novel phosphorus and nitrogen-containing diol was synthesized by Wang *et al.*, and then, introduced in alkyd resins synthesis in order to impart FR properties.¹⁹ However, possible cooperative effects between phosphorus and nitrogen were not noted.

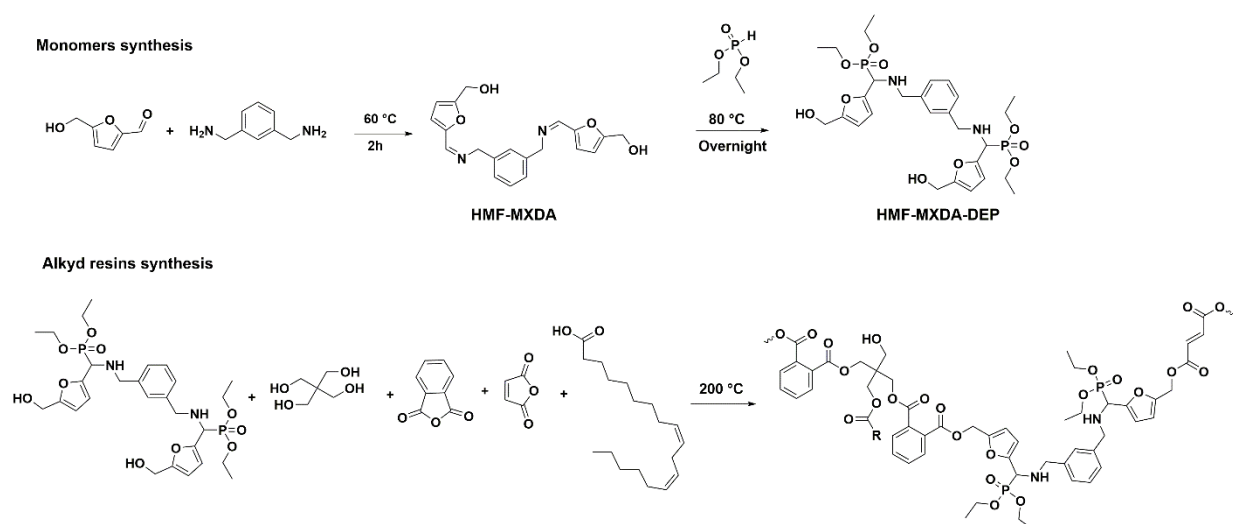
The development of reactive flame retardants based on bioresources has accelerated considerably in recent years. Environmental concerns and the issue of sustainability have been heightened with the emergence of new restrictions for the use of certain chemicals based on fossil resources. Many biomass feedstocks such as itaconic acid, eugenol, phloroglucinol are readily available, generally non-toxic and their costs do not depend on fluctuations in petrochemical markets. That is why they have been used to synthesize novel biobased FR.^{5,20-26} More recently, furan-based compounds have attracted interest in the development of FR due to their resistance to high temperatures.²⁷ Furans are five-membered conjugated heterocycles. This structure favors Diels Alder reactions during polymer degradation and the formation of a protective char layer.²⁴ The synthesis of bisfuran-based

curing agents and demonstration of their effects on increasing char residue and reducing the heat of combustion on epoxy resins has been reported.²⁴

5-Hydroxymethylfurfural (HMF), bis-2,5-(hydroxymethyl)furan (BHMF), 2,5-furandicarboxylic acid (FDCA), are commercially available furan compounds containing reactive functions for esterification reactions. Furans are usually obtained from plants derivatives and more particularly from cereals which contain starch. Indeed, starch can be hydrolyzed to generate glucose which can be converted to HMF.^{28–32} Then, HMF can be used to produce FDCA. Moreover, glucose and other carbohydrates can be a source of BHMF.^{26,33–36} Novel phosphorus and BHMf-containing FR as adducts for epoxy matrix have been reported.²⁶

Flame retardant properties of phosphorus and nitrogen based HMF which may be used as a curing agent in epoxy resins have been studied.³⁷ Good flame retardancy as a consequence of char formation was noted. The synthesis of a furfural-based DOPO-containing curing agent for epoxy resins with FR properties has been reported.³⁸ Furthermore, the combination of both nitrogen and phosphorus elements in these compounds would improve flame retardant properties and favor char formation. Indeed, it is well known that the presence of phosphorus in compounds containing high oxidation state and protonated nitrogen may display cooperative effect.³⁹

However, neither a reactive furan compound nor a phosphorus and nitrogenous furan have ever been grafted onto an alkyd resin to improve its flame retardant properties. Hence, furan compounds containing reactive functions have been condensed with organophosphorus compound to provide an efficient environmentally friendly FR (Scheme 1). This phosphorus and nitrogen-containing furan was used for the synthesis of alkyd resins. Molecular structure of the FR was characterized using nuclear magnetic resonance (NMR). The alkyd resins synthesized thereof were characterized using size exclusion chromatography (SEC). Flammability resistance properties were investigated using thermogravimetric analysis (TGA), pyrolysis combustion flow calorimeter analysis (PCFC) and cone calorimeter. Alkyd resins were applied as coatings on wood substrates for the cone calorimeter analysis. First, the thermal stability of furan based resin was investigated and then, the FR properties of phosphorus and nitrogen-containing furan based resin.



Scheme 1: General scheme of furan-based phosphorus FR for alkyd resins synthesis with flame retardant properties

2. Experimental

2.1. Materials

5-(Hydroxymethyl)furfural (HMF) was acquired from Apollo Scientist (United Kingdom). Tall oil fatty acid (TOFA), pentaerythritol, phthalic anhydride, maleic anhydride, White Spirit, calcium octoate,

zirconium octoate and cobalt octoate were kindly supplied by Lixol (Groupe Berkem, Blanquefort, France) and used as received. Potassium hydroxide (KOH), m-xylylenediamine (MXDA), diethyl phosphite (DEP), zinc chloride (ZnCl₂), xylene were purchased from Sigma Aldrich (France). Sodium chloride (NaCl), magnesium sulfate (MgSO₄), dichloromethane (DCM), tetrahydrofuran (THF), ethanol (EtOH) and ethyl acetate (EtOAc) were purchased from VWR International S.A.S (Fontenay-sous-Bois, France). The NMR solvent used was CDCl₃ from Eurisotop (United Kingdom). All reagents were used as received.

2.2 Synthesis

Synthesis of (1E,1'E)-N,N'-(1,3-phenylenebis(methylene))bis(4-(hydroxymethyl)cyclopenta-1,3) diene-1-carbimidic acid (HMF-MXDA)

In a 1000 mL three-necked round-bottomed flask equipped with a condenser, a magnetic stirring bar, a dropping funnel and a nitrogen inlet, 300 g of HMF (2.38 mol, 2 eq.) were dissolved in 500 mL of ethanol (EtOH). Then, 162 g of MXDA (1.19 mol, 1 eq.) were slowly added through the dropping funnel over 30 min. After adding, the reaction mixture was increased to 60 °C for 2 hours. Then, the solvent was removed under reduced pressure and a brown solid was obtained, with a 98 % yield (Figure 1).

¹H NMR (400 MHz, DMSO-d₆, ppm): δ = 8.22 (2H, s, H_f), 7.88-7.16 (4H, m, H_a), 6.86 (2H, d, H_b), 6.40 (2H, d, H_c), 5.37 (2H, s, OH_e), 4.69 (4H, s, H_d), 4.43 (4H, s, H_g) (Figure 3b).

HRMS (ESI+): calc. for [M + H⁺] 381.17 g.mol⁻¹, found 381.19 g.mol⁻¹.

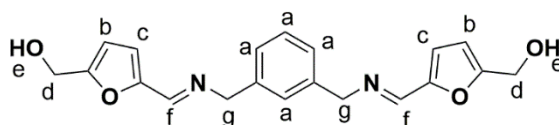


Figure 1: HMF-MXDA structure

Synthesis of diethyl (((3-(((diethoxyphosphoryl)(hydroxy)(4-(hydroxymethyl)cyclopenta-1,3-dien-1-yl)methyl)amino)methyl)benzyl)amino)(hydroxy)(4-(hydroxymethyl)cyclopenta-1,3-dien-1-yl)methyl)phosphonate (HMF-MXDA-DEP)

In a 500 mL three-necked round-bottomed flask equipped with a condenser, a magnetic stirring bar and a nitrogen inlet, 50 g of HMF-MXDA (0.13 mol, 1 eq.), 35.9 g of diethyl phosphite (0.26 mol, 2 eq.), 0.9 g of ZnCl₂ (5 mol%) and 250 mL of EtOH were added. Then, the reaction mixture was heated to 80 °C and stirred for 14 hours. After the reaction, the solvent was removed under reduced pressure and the crude product was extracted three times with dichloromethane (DCM). The organic layers were combined and washed with sodium chloride saturated solution. Finally, the organic layers were dried over MgSO₄, filtered and the DCM was removed under reduced pressure. The pure product, presented in Figure 2, was obtained as a brown viscous liquid with 88 % yield. The HMF-MXDA-DEP exhibited a phosphorus percentage of 9.4 %.

¹H NMR (400 MHz, DMSO-d₆, ppm): δ: 7.30-7.16 (4H, m, H_a), 6.38 (2H, dd, H_b), 6.26 (2H, d, H_c), 5.21 (2H, s, OH_e), 4.38 (4H, s, H_d), 4.09 (4H, m, H_g), 3.98-3.74 (8H, m, H_h), 3.53 (2H, d, H_f), 1.26-1.14 (12H, m, H_i) (Figure 3c).

³¹P NMR (161.9 MHz, DMSO-d₆, ppm): δ: 20.9 (P-C) (Figure 4b).

HRMS (ESI+): calc. for [M + H⁺] 657.65 g.mol⁻¹, found 657.62 g.mol⁻¹.

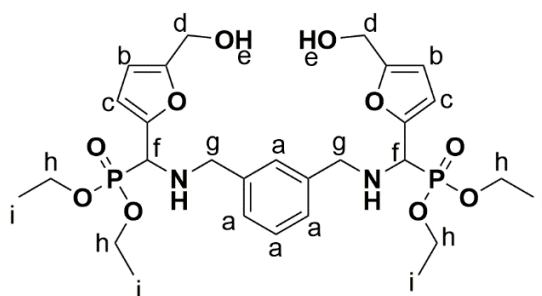


Figure 2: HMF-MXDA-DEP structure

Synthesis of alkyd resins

Long oil TOFA alkyd resins were prepared by solvent process using TOFA, phthalic anhydride, maleic anhydride, pentaerythritol and HMF-MXDA or HMF-MXDA-DEP. The amount of the reagents is presented in Table 1. TOFA was firstly added in a five necked reactor flask equipped with a mechanical stirrer, a Dean Stark, a thermometer and a nitrogen inlet. Then, when the reaction reached 150 °C, pentaerythritol and furan were added, followed by phthalic anhydride and maleic anhydride at 180 °C. The reaction mixture was heated to 185 °C using xylene as azeotropic solvent to remove water. The reaction was continued until an acid value of 10 mg of KOH/g of resin was obtained. Xylene was removed by vacuum and then White Spirit was added in order to obtain a solid content of 75 wt%. The resins have been designed to have the same oil length in their composition. The oil length is defined as the mass percentage of fatty chains on the total mass of the alkyd resin. The resins had 68 wt% of fatty acids in their composition which classified them as long oil length. The stoichiometry of f_{OH}/f_{COOH} for all the alkyd resins was maintained between 1.21 and 1.23.

Table 1: Composition of furan modified alkyd resins

Samples		Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
Wt% P		0	0	1	2
HMF-MXDA or HMF-MXDA-DEP	Mol	0.00	0.03	0.03	0.05
	f_{OH} (mol)	0.00	0.06	0.06	0.1
TOFA	Mol	0.36	0.38	0.39	0.36
	f_{COOH} (mol)	0.36	0.38	0.39	0.36
Pentaerythritol	Mol	0.24	0.20	0.20	0.13
	f_{OH} (mol)	0.96	0.80	0.80	0.52
Phthalic anhydride	Mol	0.21	0.16	0.15	0.07
	f_{COOH} (mol)	0.42	0.32	0.30	0.14
Maleic anhydride	Mol	0.005	0.005	0.005	0.005
	f_{COOH} (mol)	0.01	0.01	0.01	0.01
f_{OH} (mol)		0.96	0.86	0.86	0.62
f_{COOH} (mol)		0.79	0.71	0.70	0.51
Ratio f_{OH}/f_{COOH}		1.22	1.21	1.23	1.22

2.3 Characterizations

NMR spectroscopy

NMR samples were prepared with DMSO-d6 as solvent and the analyses were performed using a Bruker Avance 400 MHz spectrometer. The structure of the monomers was determined by hydrogen nuclear magnetic resonance (^1H NMR) and phosphorus nuclear magnetic resonance (^{31}P NMR) if necessary. External references were trimethylsilane (TMS) for ^1H and phosphoric acid (H_3PO_4) for ^{31}P NMR. Shifts were given in ppm.

Acid values (AV)

Acid values were determined according to ISO 2114:2000 standard. It is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin. Approximately, 1 g of the reaction mixture was withdrawn and solubilized in a neutralizing solution (80/20 xylene/ethanol). The solution was then titrated with a KOH solution at $0.1 \text{ mol}\cdot\text{mL}^{-1}$. Thanks to the following equation (2), the acid value was calculated.

$$AV = \frac{V_{\text{KOH}} \times M_{\text{KOH}} \times C_{\text{KOH}}}{m \times N.V.C.} \quad (2)$$

AV: Acid value; V_{KOH} : volume of KOH solution introduced to neutralize the alkyd resin (mL); M_{KOH} : molecular weight of KOH ($\text{g}\cdot\text{mol}^{-1}$); C_{KOH} : concentration of KOH ($\text{mol}\cdot\text{mL}^{-1}$); m : mass of alkyd resin withdrawn (g); N.V.C.: Non Volatile Content.

Rheological analyses

Rheological analyses were performed on a ThermoScientific Haake Mars 60 rheometer equipped with a 35-mm-cone-plate geometry. The analyses were performed at $20 \text{ }^\circ\text{C}$ with a shear rate of 10 s^{-1} . All the resins were compared at the same non-volatile content of 75 wt%.

Size-exclusion chromatography (SEC)

Molecular weights of alkyd resins were determined by size-exclusion chromatography (SEC). SEC was recorded using a triple-detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multidetector GPC calculation. The system used two PL1113-6300 ResiPore $300 \times 7.5 \text{ mm}$ columns with THF as the eluent with a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$. The detector was a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at $35 \text{ }^\circ\text{C}$. Polymethylmethacrylate (PMMA) standards were used for calibration between 540 and 2 210 000 $\text{g}\cdot\text{mol}^{-1}$. The typical sample concentration was $15 \text{ mg}\cdot\text{mL}^{-1}$.

Gel content

The resins were mixed with 5wt% of mix of driers (cobalt octoate, calcium octoate and zirconium octoate) to be crosslinked with the phosphorus reactive diluent. Then, three samples from the same alkyd resin films, of around 20 mg each, were separately immersed in THF for 24 h. The three samples were then dried in a ventilated oven at $70 \text{ }^\circ\text{C}$ for 24h. The gel content (GC) was calculated using equation (2), where m_2 is the mass of the dried material and m_1 is the initial mass. Reported gel content are average values of the three samples.

$$GC = \frac{m_2}{m_1} \times 100 \quad (2)$$

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a Netzsch DSC200F3 calorimeter. The calibration was performed using adamantane, biphenyl, indium, tin, bismuth and zinc standards. Nitrogen was used as the purge gas. The thermal properties were analyzed at $20 \text{ }^\circ\text{C}/\text{min}$ between -100 and $100 \text{ }^\circ\text{C}$ to observe the glass transition temperature.

Thermogravimetric analyses

Thermogravimetric analyses (TGA) of the cured alkyd resins were carried out to determine the thermal stability and were performed on a Netzsch TG 209F1 apparatus under 40 mL.min⁻¹ nitrogen flow. The protective gas used was nitrogen with a 20 mL.min⁻¹ flow. Approximately 10-12 mg of sample were placed in an alumina crucible and heated from room temperature to 850 °C with a 20 °C.min⁻¹ heating rate.

Pyrolysis combustion flow calorimeter analysis

Flammability of resins was analyzed using a pyrolysis combustion flow calorimeter (PCFC). About 3-4 mg were placed in the pyrolyzer, undergoing an increase of temperature from 20 °C to 750 °C at a rate of 1 °C.s⁻¹ under a nitrogen flow. Pyrolytic gases were sent to a combustor heated at 900 °C under air flow (N₂/O₂ = 80/20). At this temperature and with 20 % of oxygen, combustion was considered to be complete. Heat release rate (HRR) was determined according to oxygen depletion (Huggett's relation) as cone calorimeter test. PCFC analyses correspond to anaerobic pyrolysis followed by high temperature oxidation of decomposition products (complete combustion)⁴⁰. All samples were tested in triplicate.

Cone calorimeter test

Cone calorimeter was used to investigate the fire behavior of resins used as coating on wood specimens. The alkyd resins were applied on a pine wood sample (100*100*25 mm) in order to obtain a coating of 0.01 g.cm⁻². The samples were placed at 2.5 cm below a conic heater and isolated by rock wool. The samples were exposed to a 35 kW.m⁻² heat flux in well-ventilated conditions (air rate 24 L.s⁻¹) in the presence of a spark igniter to force the ignition. Heat release rate (HRR) was determined by oxygen depletion according to Huggett principle (1 kg of consumed oxygen corresponds to 13.1 MJ of heat released)⁴¹. Peak of Heat Release Rate (pHRR) is the maximal value of the heat release rate. The total heat released (THR) was obtained by integration of HRR curves. All samples were tested in triplicate.

Film properties

100 µm wet films were applied with a film applicator and dried at 25 °C under relative humidity of 30 %. The thickness of dry films was 75 µm in all cases. Adhesion was measured on an aluminum plate using a cross-cut tester 1 mm BYK according to ISO 2409:2020 standard and the method is explained in supporting information (SI). The hardness (Persoz hardness) was determined according to ISO 1522:2006 standard with a TQC SP0500 pendulum hardness tester (method explained in SI). Gloss was measured based on ISO 2813:2014 standard and the measurements were performed on substrates at 60° and 20° using a TQC Polygloss (method explained in SI). The color of the alkyd resins was determined using the Gardner color scale (explained in SI). The values for the hardness and the gloss measurements were determined at day +10 (D+10) after the application of the film. The drying time of the resins was considered as the time required to obtain a tack-free film. The chemical resistance of the alkyd resins was studied on water (H₂O), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl)⁴². Approximately 10 ± 1 mg of the cured alkyd resins were immersed inside each solvent during six hours at room temperature and stirred at 200 rpm. Then, they were dried in an oven at 70 °C for 12 hours. The residual mass percentage (wt% residue) was determined using equation (3). The analyses were made in triplicate for each sample and the reported residual masses percentage are average values of the three samples.

$$wt\% \text{ residue} = \frac{m_2}{m_1} \times 100 \quad (3)$$

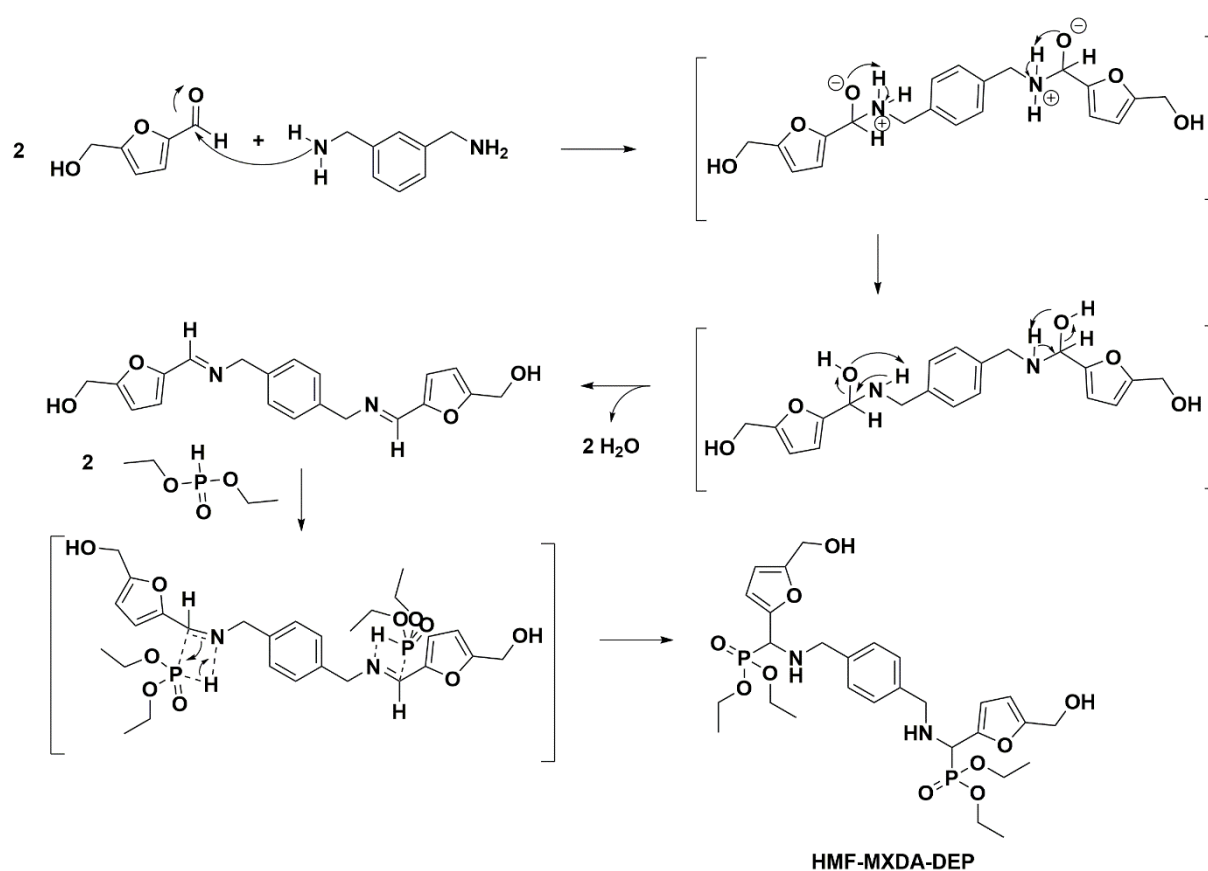
m_1 : mass of the alkyd resin sample before being immersed in solvent; m_2 : mass of the alkyd resin sample after being immersed in a solvent and dried in oven.

3. Results and discussion

1) Synthesis

Synthesis of furan diol (HMF-MXDA and HMF-MXDA-DEP)

The furan diol monomers were synthesized through the Kabachnik-Fields reaction and described in *Scheme 1*. The synthesis occurred in two steps and the mechanism has been investigated by Cherkasov *et al.*⁴³ Firstly, a Schiff base (an imine) is formed by the reaction of the carbonyl compound (HMF) and the diamine (MXDA), added in ratio 2:1, in order to form HMF-MXDA monomer. Then, the diethyl phosphite is added and reacted with the C=N bond of the HMF-MXDA. A mechanism of the reaction is proposed in *Scheme 2*.



Scheme 2: Mechanism for the HMF-MXDA-DEP formation (Kabachnik-Fields reaction)

HMF-MXDA and HMF-MXDA-DEP were characterized by ^1H and ^{31}P NMR spectroscopy (Figures 3 and 4). The disappearance of the signal at 9.40 ppm, characteristic of aldehyde function, in the ^1H NMR spectrum of HMF-MXDA (Figure 3a), and the appearance of the chemical shift at 8.22 ppm (Figure 3b) confirmed the formation of an imine function. Then, in the ^1H NMR spectrum of HMF-MXDA-DEP, the chemical shift of the imine function disappeared as well as the characteristic peak of P-H bond at 5.91 and 7.61 ppm, a doublet peak with a $J_{\text{P-H}}^1 = 680$ (Figure 3c). Moreover, the ^{31}P NMR spectrum confirmed the formation of a P-C bond with the appearance of a peak at 20.9 ppm (Figure 4b).

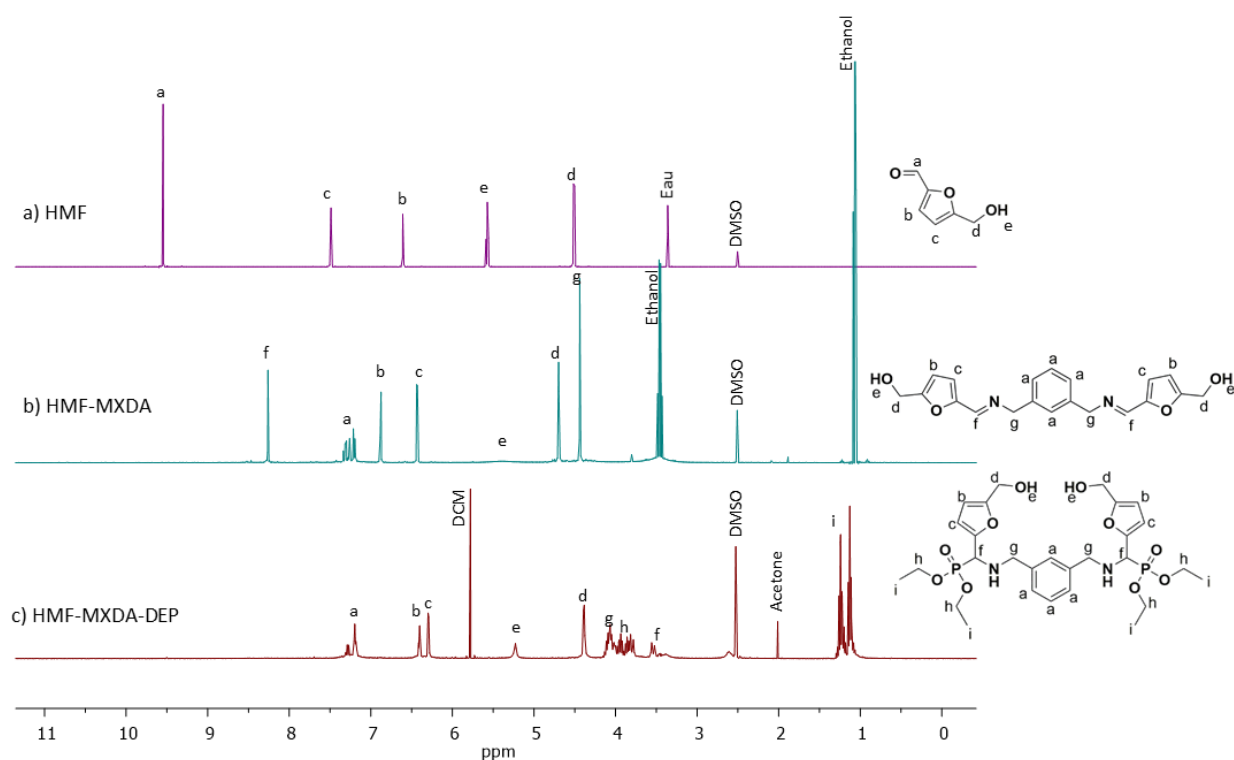


Figure 3: ^1H NMR spectra a) HMF, b) HMF-MXDA, c) HMF-MXDA-DEP (DMSO- d_6)

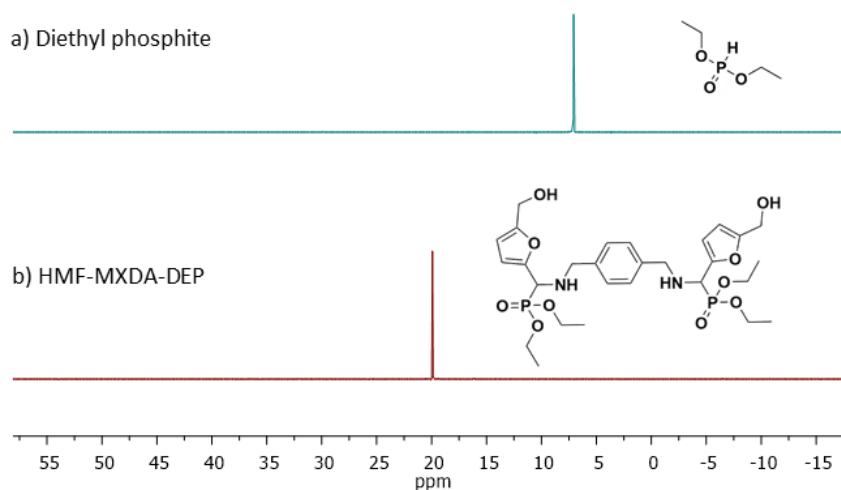
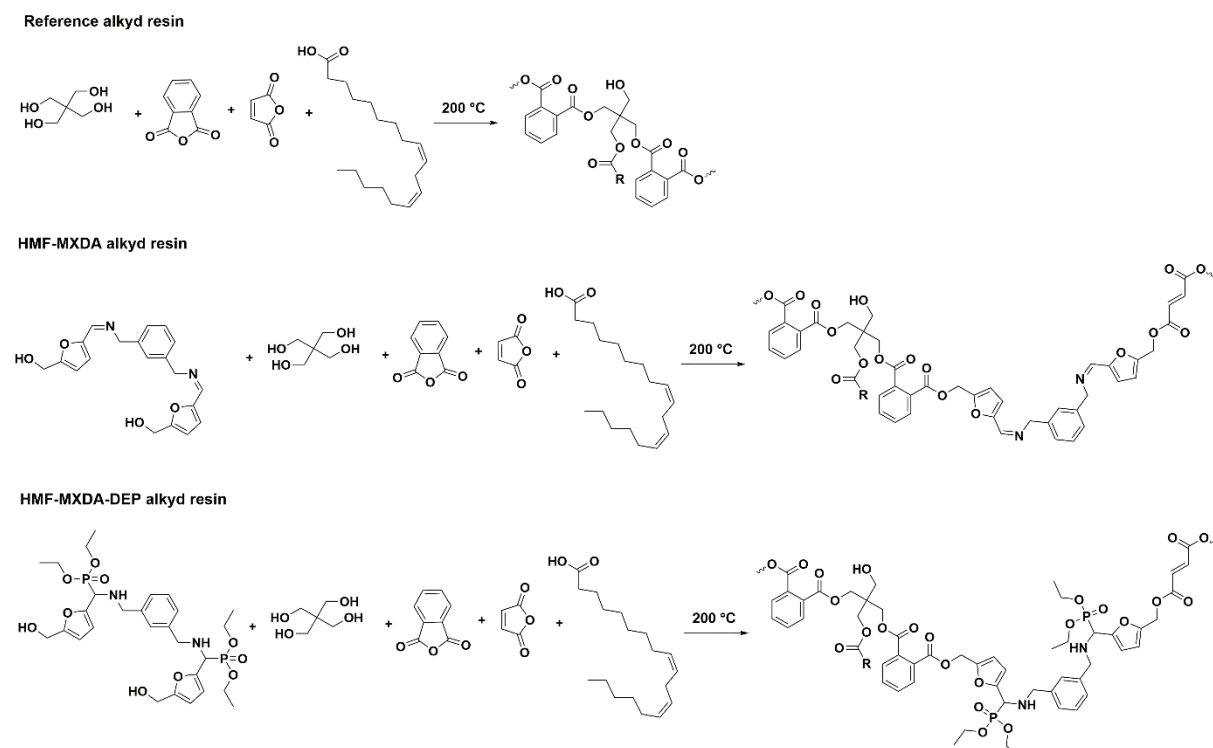


Figure 4: ^{31}P NMR spectra of a) diethyl phosphite and b) HMF-MXDA-DEP (DMSO- d_6)

Synthesis of alkyd resins containing bisfuran

In this study, alkyd resins have been synthesized through a fatty acid process with the presence of xylene as azeotropic solvent. The synthesis of tall oil fatty acid (TOFA) alkyd resin is presented in Scheme 3. The alkyd resins HMF-MXDA and HMF-MXDA-DEP 1 contain the same amount of furan. They have been synthesized in order to evaluate the thermal stability of furan and analyze the flame retardant properties of phosphonate compound. The alkyd resins HMF-MXDA-DEP 1 and HMF-MXDA-DEP 2 contain furan and diethyl phosphite with 1 m% and 2 m% P, respectively. The resins have been designed to present the same excess of hydroxyl functions and to keep a long oil length.³

All the resins had 68 wt % of fatty acids in their composition. The final acid values (AV) are presented in Table 2. It is defined as the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin. It represents the free acid groups in the resins. The progress of the reaction was monitored by the measure of AV. Indeed, the decrease of AV corresponds to advancement of step growth polymerization. The final acid value (AV) was also kept in the same range, around 7 mg KOH.g^{-1} for all the alkyd resins.



Scheme 3: Syntheses of reference alkyd resin, HMF-MXDA alkyd resin and HMF-MXDA-DEP alkyd resin

Size exclusion chromatography (SEC) allows to determine the number average molar mass M_n , the weight average molar mass M_w and the dispersity \mathcal{D} of the resins. For the reference alkyd resin, the values of weight (M_w) and number (M_n) average molar mass were respectively $14,500 \text{ g.mol}^{-1}$ and $4,000 \text{ g.mol}^{-1}$ with a high dispersity, as presented in Figure 5, which is characteristic of alkyd resins. All the alkyd resins exhibited similar M_w values compared to the reference alkyd resin (Table 2). Indeed, all the M_w values were between $13,000$ and $14,500 \text{ g.mol}^{-1}$, which are acceptable values to obtain films therefrom. All the M_n were also very similar with values between $3,000$ and $4,000 \text{ g.mol}^{-1}$. Nevertheless, even with similar M_n and M_w values, the appearance of the curves could be different, as presented in Figure 5. The alkyd resin containing HMF-MXDA showed a dispersity (\mathcal{D}) value a little higher than the other resins and the smallest M_n . This difference could be related by the intense peak between $1,000$ and $2,000 \text{ g.mol}^{-1}$ presented in Figure 5. During the polycondensation, a same small chain of oligomers with a hydroxyl function on the one hand and with an acid function on the other hand, could react on itself and then lead to the formation of cycles.⁴⁴ Those cycles have a low molar mass and they cannot longer react which explained the high dispersity of alkyd resins.⁴⁵ This phenomenon is not controlled and appears at any time during the polycondensation. That is why some alkyd resins contained more or less oligomers than others.

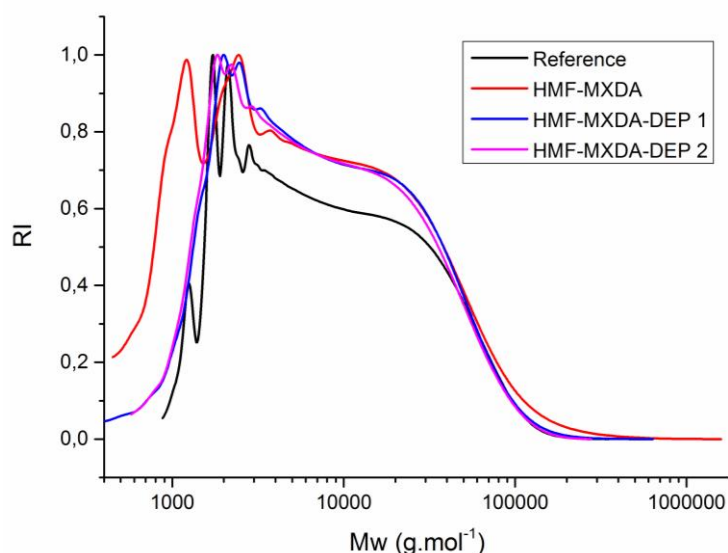


Figure 5: SEC chromatograms of alkyd resins

Table 2: Final acid value, M_n , M_w and \bar{D} results of furan modified alkyd resins

Samples	Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
Acid value (AC)	7	7	7	6
M_n ($g.mol^{-1}$)	4,000	3,000	4,000	3,500
M_w ($g.mol^{-1}$)	14,500	14,000	14,000	13,000
\bar{D}	3.4	4.7	3.6	3.5

2) Rheological and thermal analyses

Thermal and rheological properties analyses were investigated in this part to highlight the impact of furan and phosphorus on the rheological properties of the alkyd resins and the coating properties of the films.

Viscometry analyses were performed at 20 °C with a shear rate of 10 s^{-1} . All the resins were compared with the same non-volatile content of 75 wt % and the results are presented in Table 3. The viscosity of all the alkyd resins were in the same range, between 3.2 and 4.0 Pa.s, which is suitable for film applications. Those results were expected as the M_w and the M_n obtained by SEC analysis were similar.

Differential scanning calorimetry (DSC) analyses are investigated to determine the glass transition temperature (T_g), and the results are reported in Table 3. The reference resin exhibited a T_g value of 4 °C while the introduction of furan monomers increased the T_g values. As the oil length and the M_w remained the same for all the alkyd resins of this study, the increasing value of T_g may be explained by the introduction of 5 membered rings of bisfuran which conferred rigidity to the polymer. The introduction of HMF-MXDA increased the T_g value to 16 °C. Moreover, when HMF-MXDA-DEP was added, in the same molar amount moles than HMF-MXDA, the T_g value remained close (19 °C). This result allowed to confirm that phosphonate group also conferred rigidity to the materials. The higher T_g was obtained with the alkyd resin containing 2 wt% P HMF-MXDA-DEP, as expected. Indeed, this

alkyd resin exhibited the highest amount of bisfuran in the polymer chain. However, all the T_g were in the same range of values and close to room temperature. Thus, the performance of the bisfuran-modified alkyd resins could be maintained as well as the intended application.

Table 3: Viscosity and T_g of bisfuran-modified alkyd resins

Samples	Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
η (Pa.s)	3.2	3.5	3.7	4.0
T_g (°C)	4	16	19	23

The thermal stability of alkyd resins was determined by thermogravimetric analyses (TGA) under nitrogen flow. Figure 6a) shows the thermograms of the reference and bisfuran-modified alkyd resins. Thermal stability increased with the introduction of HMF-MXDA. Thermal factors such as the temperature at 5 % weight loss, the temperature at 50 % weight loss, the temperature at maximum weight loss ($T_{d,max}$) and the residue yield at 800 °C, are summarized in Table 4. First, the temperature at 5 % weight loss ($T_{d,5wt\%}$) increased by 41 °C for the HMF-MXDA-modified alkyd resin compared to the reference alkyd resin (163 vs 204 °C). The modification of HMF-MXDA with a phosphonate compound (diethyl phosphite) also increased the thermal stability. The $T_{d,5wt\%}$ value increased from 204 °C to 224 and 229 °C with the introduction of respectively 1 and 2 wt% P, compared to the HMF-MXDA-modified alkyd resin. Considering the temperature at 50 % weight loss ($T_{d,50wt\%}$) the thermal stability was higher when bisfuran compounds were introduced into alkyd resins. Indeed, $T_{d,50wt\%}$ varied from 364 °C for the reference resin to 397 °C for the HMF-MXDA alkyd resin. The thermal stability was highly improved by the introduction of HMF-MXDA-DEP compounds. The increasing amounts of phosphonate improved the $T_{d,50wt\%}$ values to 431 °C and 438 °C for the HMF-MXDA-DEP alkyd resins with 1 and 2 wt% P, respectively. The $T_{d,max}$ is presented in Figure 6b) which represents the derivatives curves of TGA. The $T_{d,max}$ increased above 450 °C with the introduction of HMF-MXDA-DEP. Globally, alkyd resins containing HMF-MXDA-DEP with 1 and 2 wt%P exhibited better thermal stability than alkyd resin containing HMF-MXDA. Those results allowed to conclude that furan groups and phosphorus compounds provide an improvement of thermal stability and that the combination of the two made further improves these properties. The residue yield at 800 °C was 3.8 wt% for the reference resin, while it reached 6.9 wt% for the resin with HMF-MXDA. Thereby, the residue yield was promoted by the amount of HMF-MXDA. Furan compounds such as HMF, are well known to be resistant to high temperatures and promote char formation through Diels-Alder reactions.²⁴ The aromatic ring of MXDA may also participate to the formation of char residue. Moreover, the residue yield increased with the introduction of diethyl phosphite, with a maximum at 12 wt% for alkyd resins with HMF-MXDA-DEP 2 wt% P. Those results were consistent with the mode of action of phosphonate compounds that act in condensed phase.^{46–48} Indeed, phosphonate compounds may decompose and participate to the formation of a char layer through cyclization, cross-linking and aromatization by dehydration of the polymeric structure.^{49,50} Then, this carbon layer could insulate the polymer and prevent heat and gas transfer between gas and condensed phases.^{51,52} Thereby, the carbon layer could protect the remaining polymer from further degradation. During decomposition, phosphorus compounds may also generate radical such as PO^\bullet . Those radicals can quench the active radicals generated by the flame (H^\bullet and OH^\bullet) and then, reduce the combustion in the gaseous phase. Nevertheless, no evidence of this gas-phase mechanism can be provided by TG analyses. Thus, the increase of both the char content and the degradation temperature is attractive for paint applications with improved thermal properties.

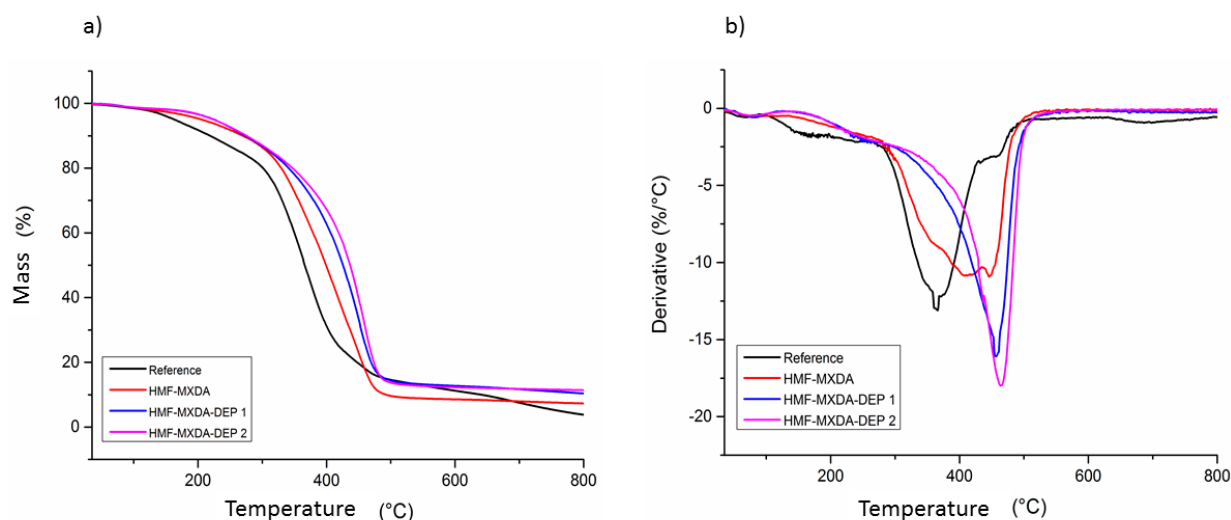


Figure 6: a) TGA curves of bisfuran-containing alkyd resins and b) DTG curves of reference alkyd resin and bisfuran-containing alkyd resins

Table 4: Results of TG analyses of bisfuran-based alkyd resins

Samples	Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
$T_{d,5wt\%}$ (°C)	163	204	224	229
$T_{d,50wt\%}$ (°C)	364	397	431	438
$T_{d,max}$ (°C)	366	423	455	458
Residue at 800°C (%)	3.8	6.9	10.6	12.0

3) Flame retardant properties

The flame retardant properties have been investigated by PCFC analysis and cone calorimeter. Table 5 summarizes the data obtained from PCFC analyses on alkyd resins. In standard conditions, combustion is complete in the PCFC test due to the high combustor chamber (900 °C) in the presence of an excess of oxygen. The total heat release (THR) and the peak of heat release rate (pHRR) are important characteristics to evaluate the flame retardant (FR) properties of a material. Figure 7 exhibits the PCFC curves of the bisfuran-modified alkyd resins. The increased amount of phosphorylated furan provided a reduction in pHRR and THR values which demonstrated the FR properties of HMF-MXDA-DEP compounds. The pHRR of the furan-free alkyd resin exhibited a value of 181 W.g⁻¹. The pHRR was slightly reduced (158 W.g⁻¹) with the introduction of bisfuran compound. Nevertheless, the addition of phosphonate into the HMF-MXDA compound, highly decreased the value of pHRR. Indeed, the pHRRs were 121 and 96 W.g⁻¹ with HMF-MXDA-DEP 1wt% P and 2 wt% P, respectively. For the same content of HMF-MXDA, the introduction of 1 wt% P decreased the pHRR by 24 % which demonstrated the remarkable efficiency of phosphonate compound onto the flame retardant properties. The best result was obtained with 2 wt% P HMF-MXDA-DEP which reduced the

pHRR by 47 % compared to the furan-free alkyd resin. The temperature of the pHRR also decreased with the introduction of phosphorylated furan. This can be attributed to an early decomposition of phosphonate. Moreover, the decomposition process is probably more complex as smaller peaks or shoulders may be observed. However, those results are contradictory with the results of the TGA analysis. For alkyd resins without phosphorus, the main peak in TGA (at « low temperature » around 360 °C) corresponds to a shoulder in the PCFC analysis. Therefore, low energy gases are released. The main peak in PCFC analysis (at higher temperature) corresponds to a weaker peak in TGA analysis so high energy gases are released. For phosphorus containing alkyd resins, the main peak in TGA at higher temperature corresponds to a weaker peak in PCFC analysis. Therefore, low energy gases are released.

The energy of complete combustion (EHC) decreased with the amount of phosphorylated furan. The residual content after anaerobic pyrolysis increased from 4 wt% to 15 wt% for the furan-free resin and the resin with HMF-MXDA-DEP 2wt% P respectively. This 11 % increase was consistent with the TGA results and demonstrated the charring promotion and furthermore, confirmed the action in condensed phase of HMF-MXDA-DEP. The excellent results obtained with nitrogen-phosphorus-furan compound (HMF-MXDA-DEP) could also be attributed to the cooperative effect P and N as demonstrated in the literature.^{39,53,54} Nevertheless, the cooperative effect P/N could not be observed because bisfuran phosphorus alkyd resin without nitrogen was not evaluated. Due to the decrease of EHC and the increase of char content, THR values decreased with increasing amounts of phosphorylated furan in alkyd resins. Indeed, the THR values were decreased from 22.3 KJ.g⁻¹ for the furan-free alkyd resin to 16.1 KJ.g⁻¹ and 14.1 KJ.g⁻¹ for the alkyd resins with HMF-MXDA-DEP 1 wt% P and 2 wt% P, respectively.

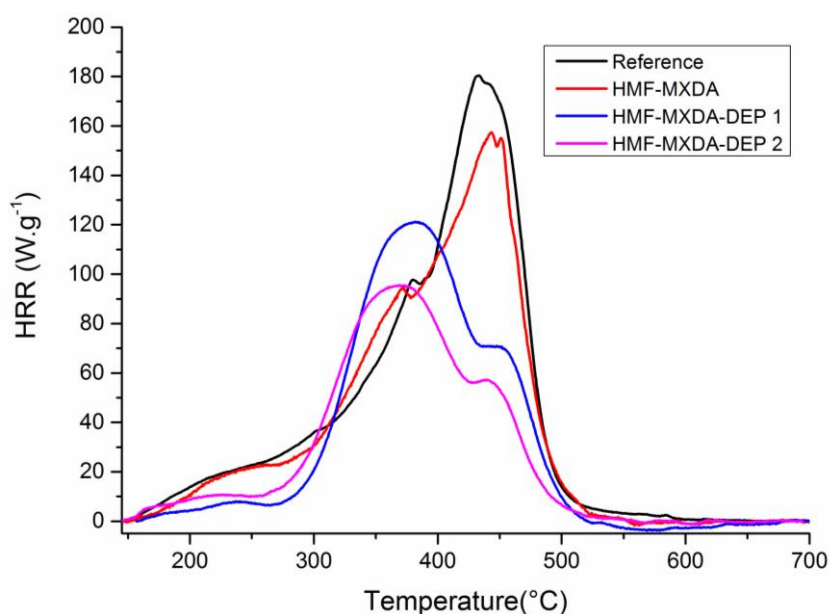


Figure 7: PCFC curves of reference alkyd resin and bisfuran-containing alkyd resins

Table 5: Results of PCFC analyses of bisfuran-modified alkyd resins

Samples	Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
pHRR (W.g ⁻¹)	181	158	121	96

<i>T at pHRR (°C)</i>	433	445	381	371
<i>THR (KJ.g⁻¹)</i>	22.3	20.5	16.1	14.1
<i>Residue content (%)</i>	4	7	12	15
<i>EHC (KJ.g⁻¹)</i>	23.2	22.0	18.3	16.6

The cone calorimeter analyses provide important information on the fire behavior of a material⁵⁵. Cone calorimeter tests were performed with a heat flux of 35 kW·m⁻² under ventilated conditions. The results are summarized in Table 6 and Figure 8 exhibited the cone calorimeter curves. Tests were performed on wood samples with around 1 g of dry resin as a coating. The rate of heat release (HRR) is important parameter to characterize the fire performance of materials. The curves (Figure 8) present two pHRR which is very common with wood samples. The first peak represents the heat release rate (pHRR₁) reached just after the ignition. After this peak corresponding to the decomposition of the top surface of wood including the coating, the heat release rate decreases until reaching a plateau which corresponds to the steady-state decomposition rate until reaching the bottom of the sample. The lower the plateau, the slower the pyrolysis front progresses through the thickness of the wood. When the heat reaches the unexposed surface (insulated by rockwool), the heat cannot be evacuated, leading to a second peak of heat release rate (pHRR₂). This second peak of heat release rate is an artefact due to the geometry of the cone calorimeter test and is independent of the coating. All the samples have a wood thickness of around 25 ± 0.2 mm.

Wood without coating presented a moderate pHRR₁ at 190 KW·m⁻² and the reference alkyd resin led to a strong enhancement of the pHRR₁ (up to 337 kW·m⁻²). Indeed, the use of a coating layer usually negatively affects the flame retardancy of wood but provides protection from external aggressions such as UV, weather, and insects. Note that the typical effective heat of combustion of wood was close to 12 kJ.g⁻¹ while the heat of combustion measured in PCFC was 23.2 kJ.g⁻¹ for the reference alkyd resin. The objective was to provide a coating with better flame retardancy than a standard coating.

The introduction of HMF-MXDA in alkyd resin slightly decreased the pHRR₁ from 337 KW·m⁻² to 299 KW·m⁻². However, when HMF-MXDA-DEP 1 wt% P was added in alkyd resin, the pHRR₁ was strongly reduced. The introduction of up to 1 wt% P phosphonate-furan compound has improved flame retardancy by decreasing the pHRR from 337 KW·m⁻² to 247 KW·m⁻². Moreover, pHRR₁ decreased with the increasing amounts of HMF-MXDA-DEP. The lower pHRR₁ was obtained with HMF-MXDA-DEP 2 wt% P in the matrix polymer which exhibited a value of 174 KW·m⁻². Indeed, pHRR₁ decreased by 49 % compared to the reference alkyd resins. This result is consistent with the decrease of pHRR obtained with PCFC analysis. Phosphorus-modified furan compounds introduced in the alkyd resins had a strong influence on the pHRR due to its ability to act in condensed phase and maybe in gas phase.

Time to ignition (TTI) measures the time to achieve sustained flaming combustion at a particular external heat flux. TTIs for all the woods with alkyd resins were lower than TTI for the uncoated wood. The bisfuran compound in the alkyl resin (TTI = 59s) increased this parameter compared to reference coating (TTI=47 s) and the amount of phosphonate introduced negatively impacted it. Indeed, alkyd resin with HMF-MXDA-DEP 1 wt% P exhibited a TTI of 56 s whereas the alkyd resin containing 2 wt% P HMF-MXDA-DEP showed a value of 46 s.

All those results confirmed the benefits of HMF-MXDA-DEP on flame retardant properties of alkyd resins. The effective heat of combustion (EHC), the total heat release (THR) and the residual mass

were not discussed because the coating only influenced $pHRR_1$ (the values are mentioned in SI Table 1).

The measurement with cone calorimeter may complete the information obtained with the previous analyses. Indeed, TGA has demonstrated the high thermal stability of bisfuran-modified alkyd resins even without phosphorus. However, cone calorimeter analysis showed that only phosphorylated bisfuran-modified alkyd resins provided flame retardant properties by strongly decreasing the heat release rate just after ignition.

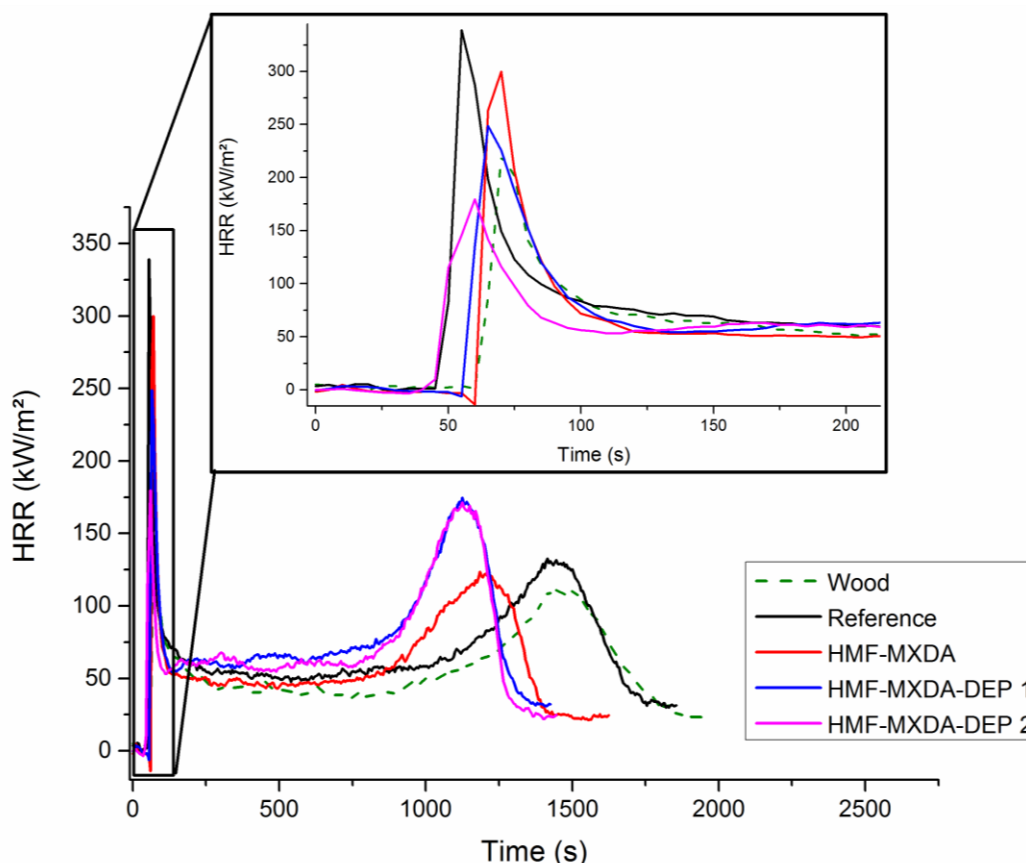


Figure 8: Curves of cone calorimeter tests for wood, reference alkyd resin and bisfuran-containing alkyd resins

Table 6: Cone calorimeter results of bisfuran-modified alkyd resins.

Samples	Wood	Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
TTI (s)	62	47	59	56	46
$pHRR_1$ (KW·m ⁻²)	218 ± 10	337 ± 9	299 ± 11	247 ± 10	174 ± 12

4) Film properties

Dry films with a thickness of 75 μm were applied from the different resins with a film applicator. Adhesion, flexibility, gloss, drying time and chemical resistance have been determined and the results are presented in the following section in table 7 and 8.

Table 7: Adhesion, hardness, gloss and drying time of bisfuran-modified alkyd resins

Samples	Reference	HMF-MXDA	HMF-MXDA-DEP 1	HMF-MXDA-DEP 2
Gel content (%)	93 ± 0.8 %	92 ± 0.6 %	91 ± 1.0 %	92 ± 0.5 %
Drying time (min)	235	280	288	282
Adhesion ^a	0	0	0	0
Hardness ^b (s)	50	51	55	61
Gloss ^c 20°/60° (G.U)	78/97	63/91	67/94	74/96
Gardner color	4	18	18	18

^a: ISO 2409:2020 standard

^b: ISO 1522:2006 standard

^c: ISO 2813:2014 standard

The gel content (GC) was determined to confirm the presence of a covalent network after drying. For all the alkyd resins, the GC were higher than 90 %, which confirms crosslinking (Table 7). All the alkyd resins showed equivalent drying times between 4 and 5 h, as expected. Indeed, all the resins exhibited M_w around 14,000 g.mol⁻¹.

The adhesion was measured by using the cross-cut method. All the alkyd resins exhibited excellent adhesion properties on aluminum substrate. The edges of the cuts were completely smooth and none of the squares of the grid were torn off, that is why they were evaluated at class 0. The introduction of HMF-MXDA and HMF-MXDA-DEP did not have impact on the adhesion properties of the resins.

The hardness of the coating was determined thanks to Persoz hardness measurement. The more flexible is the film, the faster the pendulum is damped and therefore the less oscillations are required (One second corresponds to one oscillation of the pendulum). Indeed, the more flexible is the film, the more it is able to absorb the energy of the pendulum. The number of oscillations is similar for all the alkyd resins and the films formed are all flexible.

The gloss of the coatings was first determined with a measurement at 60 ° to determine the gloss level. All the alkyd resins exhibited high gloss level with values between 91 G.U. and 97 G.U. The measurement was then made at 20 °. The reference resin showed a value of 78 G.U. whereas the gloss values were slightly modified with the introduction of HMF-MXDA and HMF-MXDA-DEP. Nevertheless, all the gloss values remained in the same range and all the alkyd resins were classified with a high gloss level. The color of all the alkyd resins was measured thanks to the Gardner color scale. The values are comprised between 1 and 18. The darker is the color, the higher is the value. The introduction of furan strongly darkened the resins with values at 18. This parameter prevents the commercialization of bisfuran-containing alkyd resins for white paint formulations. However, some applications, such as use for primer paints are unaffected by the use of dark alkyd resin. Primers are the first coat to be applied on a substrate before applying a topcoat. The primers offer many advantages such as adhesion to surfaces, protection of the substrate (anti-corrosion), or even insulation (stains, humidity, UV).

Table 7 presents the results of the determination of alkyd resins chemical resistance. The higher is the weight loss, the lower is the residual mass percentage and the less resistant is the resin to the

solvent. The synthesis of bisfuran-based alkyd resins did not deteriorate the chemical resistance of the resins. Indeed, all the bisfuran-containing alkyd resins exhibited similar chemical resistances with the reference alkyd resin. Nevertheless, a lower resistance of alkyd resins is encountered with an alkali solution (NaOH 0.1 M). This weaker resistance can be due to hydrolysable ester groups in the alkyd resins.^{29,32}

Table 8: Residual mass (%) of bisfuran-modified alkyd resins for chemical resistance

<i>Samples</i>	<i>Reference</i>	<i>HMF-MXDA</i>	<i>HMF-MXDA-DEP 1</i>	<i>HMF-MXDA-DEP 2</i>
<i>Water</i>	94 % ± 1 %	93 ± 1 %	94 ± 1 %	96 ± 2 %
<i>HCl (0.1 M)</i>	98 % ± 0,5 %	97 ± 1 %	96 ± 2 %	95 ± 3 %
<i>NaOH (0.1 M)</i>	55 % ± 3 %	57 ± 1 %	54 ± 2 %	57 ± 2 %
<i>NaCl (5 %)</i>	91 % ± 2 %	90 ± 3 %	92 ± 1 %	91 ± 2 %

4. Conclusion

A new biobased phosphorylated furan compound has been successfully synthesized and used as diol during the step growth copolymerization of hydroxyl and acid monomers for the synthesis of alkyd resins. The introduction of bisfuran compound allowed to synthesize alkyd chains with similar characteristics as the reference alkyd resin, demonstrated by SEC analysis. The film properties such as drying time, adhesion, hardness and chemical resistance were not impaired with bisfuran-based alkyd resins. However, as expected, the color was very impacted and showed values above 18 on the Gardner color scale due to the dark color of furans. However, phosphorylated bisfuran-based alkyd resins could be used for primer paints which provide a protective layer to the substrate. The fire behavior of these resins was investigated by TGA, PCFC and cone calorimeter. All alkyd resins exhibited better thermal behavior with phosphorylated furan compound. TGA and PCFC analyses have demonstrated that phosphorylated furan group acts in the condensed phase and promotes char formation. Wood protected with a coating containing 2 wt% P HMF-MXDA-DEP exhibited a 49 % reduction in pHRR compared to the furan-free coating.

5. Acknowledgement

The authors would like to thank Lixol and especially Pierre Thouzeau and Line Maibeche for their contribution to the film properties analyses.

References:

1. Hofland, A. Alkyd resins: From down and out to alive and kicking. *Progress in Organic Coatings*, **2012**, 73, 274–282.
2. La Nasa, J., Degano, I., Modugno, F., Colombini, M. P. Alkyd paints in art: Characterization using integrated mass spectrometry. *Anal. Chim. Acta*, **2013**, 797, 64–80.
3. Wicks, Z. W. Alkyd Resins. *Kirk-Othmer Encyclopedia of Chemical Technology*, **2000**, 2, 147–169.
4. Elliott, W. T. Alkyd Resins. *Surf. Coatings*, **1993**, 5, 76–109.
5. Howell, B. A., Carter, K. E., Dangalle, H. Flame Retardants Based on Tartaric Acid. *ACS Symp. Ser.*, **2011**, 1063, 133–152.
6. O’Neill, L. A. Flame-retardant paints. *Fire Mater.*, **1984**, 8, 17–19.
7. Hapuarachchi, T. D., Peijs, T. Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin. *Express Polym. Lett.*, **2009**, 3, 743–751.
8. Weil, E. D. Fire-protective and flame-retardant coatings - A state-of-the-art review. *J. Fire Sci.*, **2011**, 29, 259–296.
9. Abd El-Wahab, H., Abd El-Fattah, M., Abd El-Khalik, N., Kazlauciuonas, A. Synthesis and performance of new modified reactive flame-retardant alkyd resin based on tetrabromophthalic anhydride as varnish for surface coatings. *Journal of Coatings Technology and Research*, **2014**, 12, 97–105.
10. Jia, P., Hu, L., Zhang, M., Feng, G., Zhou, Y. Phosphorus containing castor oil based derivatives: Potential non-migratory flame retardant plasticizer. *Eur. Polym. J.*, **2017**, 87, 209–220.
11. Gündüz, G., Kisakürek, D., Kayadan, S. Flame retardant alkyd paint. *Polymer Degradation and Stability*, **1999**, 64, 501–504.
12. Ikhuoria, E. U. *et al.* Synthesis and characterisation of chlorinated rubber seed oil alkyd resins. *Progress in Organic Coatings*, **2007**, 59, 134–137.
13. Spatz, S. M., Stone, H., Koral, M., Steiner, R. I., Ackerman, H. W. Use of tetrabromophthalic anhydride (tbpa) in the construction of fire-retardant polyester and epoxy resins. *Industrial and Engineering Chemistry Product Research and Development*, **1969**, 8, 381–391.
14. Cui, J., Chen, B., Guo, J., Zhou, Y., Yang, B. Preparation of bromine carbon alkyd resin retardant coatings for steel structure. *Applied Mechanics and Materials*, **2013**, 275, 1921–1924.
15. Frigione, M., Maffezzoli, A., Finocchiaro, P., Failla, S. Cure Kinetics and Properties of Epoxy Resins Containing a Phosphorous-Based Flame Retardant. *Adv. Polym. Technol.*, **2003**, 22, 329–342.
16. Van Der Veen, I., De Boer, J. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, **2012**, 88, 1119–1153.
17. Zhang, C., Huang, J. Y., Liu, S. M., Zhao, J. Q. The synthesis and properties of a reactive flame-retardant unsaturated polyester resin from a phosphorus-containing diacid. *Polym. Adv. Technol.*, **2011**, 22, 1768–1777.
18. Zhang, C., Liu, S. M., Zhao, J. Q., Huang, J. Y. Synthesis and properties of a modified unsaturated polyester resin with phosphorus-containing pendant groups. *Polym. Bull.*, **2013**, 70, 1097–1111.
19. Wang, Y. *et al.* Chemical modification of alkyd resin by a DOPO derivative and its flame retardancy. *Journal of Applied Polymer Science*, **2018**, 135, 45643.
20. Howell, B. A., Daniel, Y. G., Ostrander, E. A. Flame Retardants from Renewable Sources: Food Waste, Plant Oils, and Starch. *Green Polym. Chem.*, **2018**, Chapter 25, 405–421.
21. Ecochard, Y., Decostanzi, M., Negrell, C., Sonnier, R., Caillol, S. Cardanol and eugenol based flame retardant epoxy monomers for thermostable networks. *Molecules*, **2019**, 24, 1818.
22. Ménard, R., Negrell, C., Ferry, L., Sonnier, R., David, G. Synthesis of biobased phosphorus-containing flame retardants for epoxy thermosets comparison of additive and reactive approaches. *Polymer Degradation and Stability*, **2015**, 120, 300–312.

23. Ménard, R., Negrell-Guirao, C., Ferry, L., Sonnier, R. & David, G. Synthesis of biobased phosphate flame retardants. *Pure and Applied Chemistry*, **2014**, 86, 1637–1650.
24. Ménard, R., Negrell, C., Fache, M., Ferry, L., Sonnier, R., David, D., From a bio-based phosphorus-containing epoxy monomer to fully bio-based flame-retardant thermosets. *RSC Advances*, **2015**, 5, 70856–70867.
25. Howell, B. A., Alomari, M. R., Dumitrascu, A., Opperman, R. S. Properties of the Phosphoramidate Derived from Chitosan and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. in *40th Annual Conference of NATAS, North American Thermal Analysis Society*, **2012**.
26. Howell, B. A., Han, X. Effective Biobased Phosphorus Flame Retardants from Starch-Derived bis-2,5-(Hydroxymethyl)Furan. *Molecules*, **2020**, 25, 592.
27. Sonnier, R., Otazaghine, B., Dumazert, L., Ménard, R., Viretto, A., Dumas, L., Bonnaud, L., Dubois, P., Safronava, N., Walters, R., Lyon, R., Prediction of thermosets flammability using a model based on group contributions. *Polymer (Guildf.)*, **2017**, 127, 203–213.
28. Howell, B. A., Daniel, Y. G. Thermal degradation of phosphorus esters derived from isosorbide and 10-undecenoic acid. *J. Therm. Anal. Calorim.*, **2015**, 121, 411–419.
29. Corma, A., Iborra, S., Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *ChemInform*, **2007**, 107, 2411–2502.
30. Teong, S. P., Yi, G., Zhang, Y. Hydroxymethylfurfural production from bioresources: Past, present and future. *Green Chem.*, **2014**, 16, 2015–2026.
31. Van Putten, R.-J., Van der Waal, J., De Jong, E., Rasrendra, C. B., Heeres, H. J., Vries, J. G., Hydroxymethylfurfural, A versatile platform chemical made from renewable resources. *Chem. Rev.*, **2013**, 113, 1499–1597.
32. Wang, T., Nolte, M. W., Shanks, B. H. Catalytic dehydration of C6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. *Green Chemistry*, **2014**, 16, 548–572.
33. Jiang, Y., Woortman, A. J. J., Alberda Van Ekenstein, G. O. R., Petrović, D. M., Loos, K. Enzymatic synthesis of biobased polyesters using 2,5-bis(hydroxymethyl) furan as the building block. *Biomacromolecules*, **2014**, 15, 2482–2493.
34. Zeng, C., Seino, H., Ren, J., Hatanaka, K., Yoshie, N. Bio-based furan polymers with self-healing ability. *Macromolecules*, **2013**, 46, 1794–1802.
35. Zhang, Y., Li, T., Xie, Z., Han, J., Xu, J., Guo, B., Synthesis and Properties of Biobased Multiblock Polyesters Containing Poly(2,5-furandimethylene succinate) and Poly(butylene succinate) Blocks. *Ind. Eng. Chem. Res.*, **2017**, 56, 3937–3946.
36. Choi, E. H., Lee, J., Son, S. U., Song, C. Biomass-Derived Furanic Polycarbonates: Mild Synthesis and Control of the Glass Transition Temperature. *Polym. Chem.*, **2019**, 57, 1796–1800.
37. Toan, M., Park, J.-W., Kim, H.-J., Shin, S. Synthesis and characterization of a new phosphorus-containing furan-based epoxy curing agent as a flame retardant. *Fire*, **2019**, 1–8.
38. Xie, W., Huang, S., Tang, D., Liu, S., Zhao, J. Synthesis of a furfural-based DOPO-containing co-curing agent for fire-safe epoxy resins. *RSC Adv.*, **2020**, 10, 1956–1965.
39. Leu, T. S., Wang, C. S. Synergistic Effect of a Phosphorus-Nitrogen Flame Retardant on Engineering Plastics. *J. Appl. Polym. Sci.*, **2004**, 92, 410–417.
40. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J. M., Dubois, P. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Materials Science and Engineering R: Reports*, **2009**, 63, 100–125.
41. Huggett, C. Estimation of rate of heat release by means of oxygen consumption measurements. *Fire Mater.*, **1980**, 4, 61–65.
42. Islam, M. R., Beg, M. D. H., Jamari, S. S. Alkyd based resin from non-drying oil. in *Procedia Engineering*, **2014**, 90, 78–88.
43. Cherkasov, R. A., Galkin, V. I. The Kabachnik Fields reaction: synthetic potential and the problem of the mechanism. *Russ. Chem. Rev.*, **1998**, 67, 940–968.
44. Mori, S., Barth, H. G. *Size Exclusion Chromatography*. Springer Berlin Heidelberg, **1999**.
45. Kricheldorf, H. R. Cyclic and multicyclic polymers by three-dimensional polycondensation.

- Accounts of Chemical Research*, 2009, 42, 981–992.
46. Schartel, B. Phosphorus-based flame retardancy mechanisms-old hat or a starting point for future development? *Materials*, **2010**, 3, 4710–4745.
 47. Braun, U., Balabonovich, A. I., Schartel, B., Knoll, U., Artner, J., Ciesielski, M., Döring, M., Perez, R., Sandler, J. K. W., Altstädt, Hoffmann, T., Pospiech, D., Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites. *Polymer*, **2006**, 47, 8495–8508.
 48. Velencoso, M. M., Battig, A., Markwart, J. C., Schartel, B., Wurm, F. R. Molecular Firefighting – How Modern Phosphorus Chemistry Can Help Solve the Flame Retardancy. *Angew. Chemie Int. Ed.*, **2018**, 57, 10450–10467.
 49. Röchow, E. T., Häußler, L., Korwitz, A., Pospiech, D. Thermal decomposition of phosphonate-containing methacrylate based copolymers. *Polym. Degrad. Stab.*, **2018**, 152, 235–243.
 50. Liang, S., Neisius, M., Mispreuve, H., Naescher, R., Gaan, S. Flame retardancy and thermal decomposition of flexible polyurethane foams: Structural influence of organophosphorus compounds. *Polym. Degrad. Stab.*, **2012**, 97, 2428–2440.
 51. Qi, J., Wen, Q., Zhu, W. Research progress on flame-retarded silicone rubber. in *Conf. Ser.: Mater. Sci. Eng.*, **2018**, 392, 032007.
 52. Hamdani, S., Longuet, C., Perrin, D., Lopez-cuesta, J. M., Ganachaud, F. Flame retardancy of silicone-based materials. *Polymer Degradation and Stability*, **2009**, 94, 465–495.
 53. Vothi, H., Nguyen, C., Pham, L. H., Hoang, D., Kim, J. Novel Nitrogen-Phosphorus Flame Retardant Based on Phosphoramidate: Thermal Stability and Flame Retardancy. *ACS Omega*, **2019**, 4, 17791–17797.
 54. Li, Q., Jiang, P., Su, Z., Wei, P., Wang, G., Tang, X., Synergistic effect of phosphorus, nitrogen, and silicon on flame-retardant properties and char yield in polypropylene. *J. Anal. Appl. Pyrolysis*, **2005**, 96, 854–860.
 55. McNally, T., Pötschke, P., Halley, P., Murphy, M., Martin, D., Bell, S. E. J., Brennan, G. P., Bein, D., Lemoine, P., Quinn, J. P., Polyethylene multiwalled carbon nanotube composites. *Polymer*, **2005**, 46, 8222–8232.