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# How phosphinated hydroxyurethane groups improve chemical resistance and flame retardant properties of alkyd resins?

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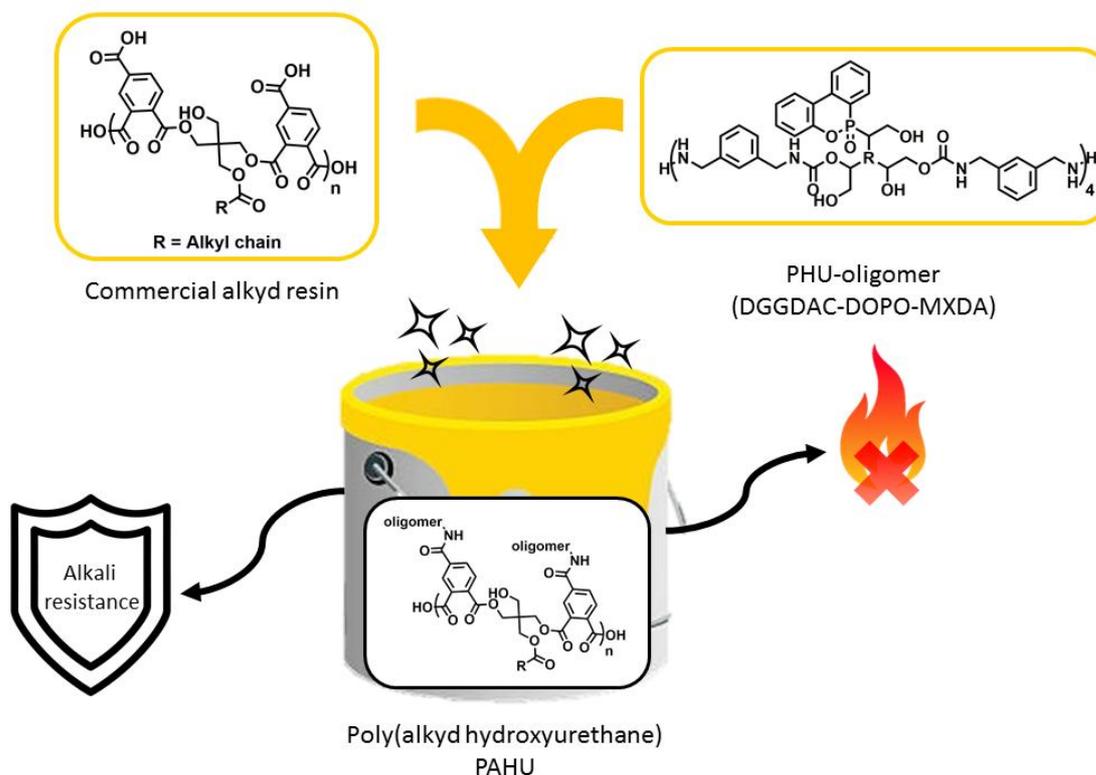
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## Graphical abstract



## Abstract

A novel phosphorus containing polyhydroxyurethane (PHU) oligomer (DGGDAC-MXDA-DOPO), has been synthesized and grafted onto the remaining acid groups of alkyd resins in order to obtain hybrid poly(alkyd hydroxyurethane) (PAHU) resins with flame retardant properties. PAHU resins have demonstrated better alkali resistance than pure alkyd resins without PHU oligomer. Moreover, the grafting of PHU onto alkyd resin through the formation of amide bonds has exhibited thixotropic properties. The thermal and flame retardancy properties have been investigated through differential scanning calorimeter, thermogravimetric analysis and pyrolysis-combustion flow calorimeter. The alkyd resins were applied as a coating on a wood surface and fire behavior was tested by cone calorimeter analysis. The most effective coating, by taking into account, the film properties and the flame retardant behavior contains 24 wt% of PHU (1.5 wt% P) and exhibited a 40 % reduction in peak of Heat Release Rate (pHRR) compared to the resins without PHU.

## Keywords

Alkyd resins, polyhydroxyurethane, poly(alkyd hydroxyurethane), hybrid resin, flame retardant

### 1. Introduction

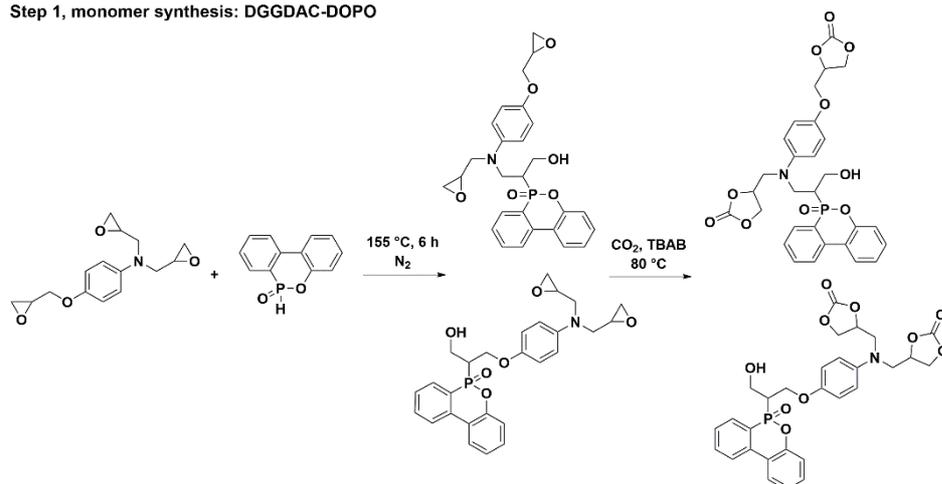
Polyesters modified with unsaturated fatty acids, named alkyd resins (AR), are used as coatings or binders in paints or varnishes formulations.<sup>1-3</sup> They can be used on a broad range of substrates such as metal or wood in various environments. They sometimes require special properties such as abrasion, UV and chemical resistance which can be essential for outdoor applications.<sup>4,5</sup> One major limitation of alkyd resins is their poor resistance to alkali environment which limits their use in marine paints. Indeed, marine paints can be used on infrastructures near the sea such as harbor zone and require a good resistance to alkali solutions. To overcome this limitation, ARs can be modified with isocyanates, leading to hybrid alkyd-urethane, named poly(alkyd-urethane) (PAU) or uralkyds, which combine the properties of both polymers.<sup>6-8</sup>

The PAU resins have demonstrated good chemical resistance in various conditions, in particular in alkaline solutions.<sup>6,7,9-12</sup> They can be obtained by various processes. Some authors have studied the synthesis of traditional alkyd resins and then the grafting of polyisocyanate compounds onto the remaining hydroxyl functions which then acted as cross-linker of alkyd chains.<sup>7,9,11</sup> Another study, of Ling *et al.* has reported the copolymerization of isocyanates with the hydroxyl monomers of alkyd resin to yield urethane functions in the main chain.<sup>12</sup> The synthesis of alkyd-urethane resins is also widespread in the coatings industry and these are generally used as top-coat to provide several properties such as better chemical resistance, protection against corrosion, UVs or humidity.<sup>6,7</sup> Isocyanate monomers such as toluene diisocyanate (TDI) or methylene diphenyl 4,4'-diisocyanate (MDI) are directly mixed with the alkyd resin just before its application, in order to form a two-component formulations (called 2K). Isocyanates can easily react at room temperature with excess hydroxyl functions and thus form PAU coating films.<sup>7</sup> The films obtained exhibit good anti-corrosion properties and resistance to aqueous, acidic and alkaline solutions. However, all these PAU resins were synthesized from isocyanates which are toxic substances, even classified as carcinogenic mutagenic and reprotoxic (CMR) in the case of MDI and TDI.<sup>9,13</sup> Consequently, recent regulations are pushing to replace them and more sustainable alternatives are gaining increasing attention.<sup>14,15</sup> For several years, to replace isocyanates, studies focused on the development of Non-Isocyanate PolyUrethanes (NIPU).<sup>14,16-18</sup> Among the various possible routes, the synthesis of polyhydroxyurethanes (PHU), resulting from the reaction of cyclic carbonate monomers and diamines, is one of the most promising routes.<sup>19-22</sup> However, only few carbonate monomers are commercially available and most of them are very expensive. Fortunately, they can be easily obtained by carbonation of the oxirane groups with carbon dioxide (CO<sub>2</sub>) under slight pressure. Moreover, this synthesis allows to valorize a waste product in large amount: the CO<sub>2</sub>. Haniffa *et al.* explored the formation of PHU alkyd resins.<sup>23</sup> Hence, they perform epoxidation of double bonds of the fatty acids of alkyd resins prior carbonation with CO<sub>2</sub>. Poly(alkyd-hydroxyurethane) (PAHU) was finally obtained during crosslinking by reacting the carbonated alkyd resin with diamines. The films obtained showed good chemical resistance to water, acid and alkaline solutions. Thus, the introduction of PHU in alkyd resins improved their resistance to alkaline solution while avoiding the use of harmful isocyanates. Nevertheless, the crosslinking reaction was not investigated by the authors and the drying time of films could have been negatively impacted since the auto-oxidative reactions of double bonds of fatty chains are needed to form a 3D network.<sup>24-27</sup> Moreover, some infrastructures such as public building near the sea, additionally to alkali resistance, require a protection against flammability. Therefore, flame retardants (FR) are incorporated in order to confer flame retardant properties and reduce the risk associated with their flammability.<sup>28</sup>

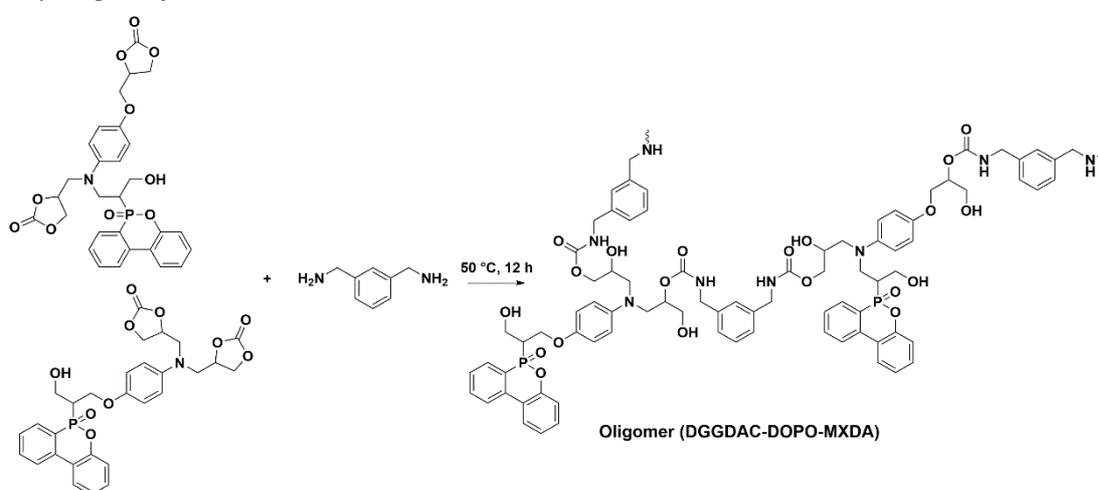
Thereby, reactive phosphorus-based FRs are the most promising route to protect alkyd resins from combustion and avoid the use of halogen flame retardants. Recently, a study of our group has demonstrated the efficiency of 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), used in the synthesis of an oligomer containing silicon (DOPO-VMDMS) that was grafted to alkyd resins.<sup>29</sup> The most interesting result has been obtained with a coating containing 30 wt% DOPO-VMDMS with a 55 % reduction in the peak of heat release rate (pHRR) compared to the FR-free alkyd resin. Moreover, the authors have shown that the film properties of the coatings were improved thanks to the hybridization with siloxane compounds.

However, there are no study showing both an improvement in the chemical resistance of alkyd resins by hybridization and the introduction of flame retardant properties. A recent study has shown the possibility of bringing flame retardant properties to PHUs by reacting phosphorus molecules having P-H bonds with epoxy compounds before carbonation of the remaining oxirane groups.<sup>30</sup> The synthesis of 4-((4-(3-hydroxy-2-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)propyl)(2-oxo-1,3-dioxolan-4-yl)methyl)amino)phenoxy)methyl)-1,3-dioxolan-2-one (DGGDAC-DOPO), is promising for the formation of reactive phosphorus PHU oligomers which can be introduced in alkyd resins to obtain PAHU with flame retardant properties. Moreover, the aromatic ring of the epoxy can promote the char formation and the nitrogen associated with phosphorus may allow a synergy. Hence, in this study, PHU oligomers with reactive functions were reacted with alkyd resins containing excess acid functions (Scheme 1). Molecular structures of the FR were characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). Alkyd resins were characterized by size exclusion chromatography (SEC), rheological analyses and FTIR. The fire proofing properties were investigated by thermogravimetric analysis (TGA), pyrolysis combustion flow calorimeter analysis (PCFC) and cone calorimeter. Alkyd resins were applied as coatings on wood supports for the cone calorimeter analysis. The film properties and the chemical resistance were also investigated.

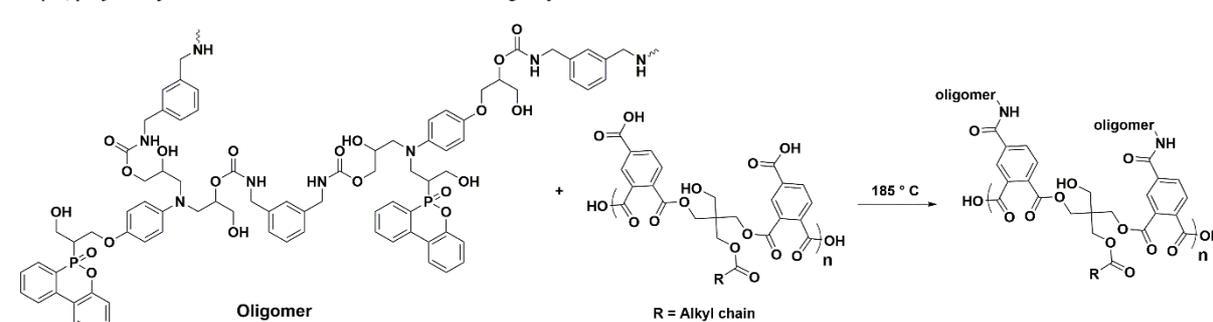
### Step 1, monomer synthesis: DGGDAC-DOPO



### Step 2, oligomer synthesis: DGGDAC-DOPO-MXDA



### Step 3, polymer synthesis: DGGDAC-DOPO-MXDA containing alkyd resin



Scheme 1: General scheme of poly(alkyd hydroxyurethane) resins with flame retardant properties

## 2. Material and methods

### 1) Materials

Tall oil fatty acid (TOFA), glycerol, phthalic anhydride, mix of driers (a solution containing cobalt octoate, calcium octoate and zirconium octoate) and an alkyd resin with acid functions in excess were kindly supplied by Lixol (Groupe Berkem, Blanquefort, France). 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was acquired from TCI. N,N-Diglycidyl-4-glycidyl-oxyaniline (DGGDA), tetrabutylammonium bromide (TBAB) (purity 99 %), *m*-xylylenediamine (MXDA) and xylene were purchased from Sigma Aldrich. Sodium chloride (NaCl), magnesium sulfate ( $\text{MgSO}_4$ ),

dichloromethane (DCM) and tetrahydrofuran (THF) were purchased from VWR International S.A.S (Fontenay-sous-Bois, France). CO<sub>2</sub> was acquired from Air Liquide. The NMR solvents used was DMSO-d<sub>6</sub> and THF-d<sub>8</sub> from Eurisotop. All reagents were used as received.

## 2) Characterizations

### Nuclear Magnetic Resonance

NMR samples were prepared with DMSO-d<sub>6</sub> as solvent and the analyses were performed using a Bruker Avance 400 MHz spectrometer at 25 °C. The structure of monomers was determined by hydrogen nuclear magnetic resonance (<sup>1</sup>H NMR), and phosphorus nuclear magnetic resonance (<sup>31</sup>P NMR). The <sup>1</sup>H NMR spectra were recorded at 8 kHz for spectral width, 3 kHz for transmitter frequency offset, 4 seconds for acquisition time and 8 scans were performed. Quantitative conditions were obtained with a 30° pulse (3 μs) and a relaxation delay at 1 second. The <sup>31</sup>P NMR spectra were recorded at 64 kHz for spectral width, 8000 Hz for transmitter frequency offset, 1 second for acquisition time and 4 scans were performed. Quantitative conditions were obtained with a 30° pulse (2.7 μs) and a relaxation delay at 20 seconds. Diffusion ordered spectroscopy (DOSY) <sup>1</sup>H NMR was used to confirm the grafting of DGGDAC-DOPO-MXDA oligomer to the alkyd resin and were performed on a Bruker Avance 500 MHz spectrometer with CDCl<sub>3</sub> as solvent. External references were trimethylsilane (TMS) for <sup>1</sup>H and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) for <sup>31</sup>P NMR. Shifts were given in ppm.

### Titration of the epoxy equivalent weight by <sup>1</sup>H NMR

The Epoxy Equivalent Weight (EEW) is the amount of product needed for one equivalent of reactive epoxy function. It was determined by <sup>1</sup>H NMR using and internal standard (benzophenone). A known mass of product and benzophenone were poured into an NMR tube and 550 μL of CDCl<sub>3</sub> were added. The EEW was determined using equation (1) by comparing the integration value of the signals assigned to the benzophenone protons (7.5-7.8 ppm) with the integration of the signals arising from epoxy protons (2.57 ppm).

$$EEW = \frac{\int PhCOPh \times H_{epoxy}}{\int epoxy \times H_{PhCOPh}} \times \frac{m_{epoxy}}{m_{PhCOPh}} \times M_{PhCOPh} \quad (1)$$

∫<sub>PhCOPh</sub>: integration of the signal from benzophenone protons; ∫<sub>epoxy</sub>: integration of the signals from protons in α epoxy function; H<sub>epoxy</sub>: number of protons in α of the epoxy function; H<sub>PhCOPh</sub>: number of benzophenone protons; m<sub>epoxy</sub>: epoxy mass; m<sub>PhCOPh</sub>: benzophenone mass; M<sub>PhCOPh</sub>: benzophenone molar mass.

### Titration of the carbonate equivalent weight by <sup>1</sup>H NMR

The Carbonate Equivalent Weight (CEW) is the amount of product needed for one equivalent of reactive cyclic carbonate function. It was determined by <sup>1</sup>H NMR using and internal standard (benzophenone). A known mass of product and benzophenone were poured into an NMR tube and 550 μL of CDCl<sub>3</sub> were added. The CEW was determined using equation (2) by comparing the integration value of the signals assigned to the benzophenone protons (7.5-7.8 ppm) with the integration of the signals arising from cyclic carbonate (5.02 plus 5.14 for DDGDAC).

$$CEW = \frac{\int PhCOPh \times H_{carbonate}}{\int carbonate \times H_{PhCOPh}} \times \frac{m_{carbonate}}{m_{PhCOPh}} \times M_{PhCOPh} \quad (2)$$

∫<sub>PhCOPh</sub>: integration of the signal from benzophenone protons; ∫<sub>carbonate</sub>: integration of the signals from protons in α the carbonate function; H<sub>carbonate</sub>: number of protons in α of the carbonate function;

$H_{\text{PhCOPh}}$ : number of benzophenone protons;  $m_{\text{carbonate}}$ : product mass;  $m_{\text{PhCOPh}}$ : benzophenone mass;  $M_{\text{PhCOPh}}$ : benzophenone molar mass.

### FTIR spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra were acquired on a ThermoScientific Nicolet iS50 FT-IR equipped with an attenuated total reflectance cell (ATR). The data were analyzed using the software OMNIC Series 8.2 from ThermoScientific.

### Inductively coupled plasma atomic emission spectrometry (ICP-AES)

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a destructive technique used to determine the elemental composition of a material. The samples have undergone a preliminary mineralization step before analysis. For this, 50 mg of compound were mixed with 1 ml of nitric acid (63%) and 2 ml of sulfuric acid (98%) in a Teflon<sup>®</sup> container. The mixture was heated by microwaves with powers ranging between 400 and 700 W following an appropriate cycle. After cooling, the mineralized solutions were then diluted with demineralized water to 50 ml before analysis by ICP-AES. During this step, the vaporized solution passed into the plasma chamber at 6000 °C and the excited atoms emit spectra specific to each element. The intensity of the peak of the phosphorus element was converted to a mass percentage using a calibration curve. Each sample was analyzed twice according to the reproducibility of measurements.

### Acid values (AV)

Acid values were determined according to ISO 2114: 2000 standard. It corresponds to the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin mass. 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 mol.mL<sup>-1</sup>. Thanks to the following equation (3), the acid value was calculated.

$$AV = \frac{V_{\text{KOH}} \times M_{\text{KOH}} \times C_{\text{KOH}}}{m \times N.V.C.} \quad (3)$$

*AV*: Acid value;  $V_{\text{KOH}}$ : volume of KOH solution introduced to neutralize the alkyd resin (mL);  $M_{\text{KOH}}$ : molar mass of KOH (g.mol<sup>-1</sup>);  $C_{\text{KOH}}$ : concentration of KOH (mol.mL<sup>-1</sup>);  $m$ : mass of alkyd resin withdraw (g); *N.V.C.*: Non Volatile Content of the sampled resin.

### 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 °C with a shear rate of 10 s<sup>-1</sup> to determine the viscosity of alkyd resins. Then, to investigate the thixotropic properties, the analyses were performed at 20 °C with a shear rate increasing from 0.1 to 100 s<sup>-1</sup> and then decreasing to 0.1 s<sup>-1</sup> to form a loop.

### Size-exclusion chromatography (SEC)

Molar masses of DGGDAC-DOPO-MXDA oligomer and alkyd resins were determined by size-exclusion chromatography (SEC). SEC was recorded using a double detection GPC from Varian ProStar 210 pump. The detector was a Shodex refractive index detector. The system used two PL1113-6300 ResiPore 300 × 7.5 mm columns with dimethylformamide as the eluent with a flow rate of 0.8 mL.min<sup>-1</sup>. The columns were thermostated at 70 °C to obtain a suitable viscosity of DMF. Polymethylmethacrylate (PMMA) standards were used for calibration between 560 and 1 568 000 g.mol<sup>-1</sup>. The typical sample concentration was 15 mg.mL<sup>-1</sup>.

### **Gel content**

The resins were mixed with 5wt% of mix of driers (cobalt octoate, calcium octoate and zirconium octoate) in order to crosslink them 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 °C for 24h. The gel content (GC) was calculated using equation (4), 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.

$$GC = \frac{m_2}{m_1} \times 100 \quad (4)$$

### **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 °C/min between -100 and 100 °C.

### **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<sup>-1</sup> nitrogen flow. The protective gas used was nitrogen with a 20 mL.min<sup>-1</sup> flow. Approximately 10 mg of sample were placed in an alumina crucible and heated from room temperature to 850°C with a 20°C.min<sup>-1</sup> 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 100 °C to 750 °C at a rate of 1 °C.s<sup>-1</sup> under a nitrogen flow. Pyrolytic gases were sent to a combustor heated at 900 °C under air flow (N<sub>2</sub>/O<sub>2</sub> = 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 in cone calorimeter test. PCFC analyses correspond to anaerobic pyrolysis followed by high temperature oxidation of decomposition products (complete combustion)<sup>31</sup>. All samples were tested in triplicate.

### **Cone calorimeter test**

Cone calorimeter tests were carried out in order 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), with a density of 500 kg.m<sup>-3</sup>, to obtain a coating of 0.01 g.cm<sup>-2</sup>. 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<sup>-2</sup> heat flux in well-ventilated conditions (air rate 24 L.s<sup>-1</sup>) 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)<sup>32</sup>. 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 80 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 taken as the time required to obtain a tack-free film. The chemical resistance of the alkyd resins was studied on water (H<sub>2</sub>O), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl)<sup>33</sup>. 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 80 °C for 12 hours. The residual mass percentage (wt% residue) was determined using equation (5). The analyses were made in triplicate for each sample and the reported residual masses percentages are average values of the three samples.

$$wt\% \text{ residue} = \frac{m_2}{m_1} \times 100 \quad (5)$$

$m_1$ : 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) Synthesis

#### Synthesis of 6-(1-hydroxy-3-((4-(oxiran-2-ylmethoxy)phenyl)(oxiran-2-ylmethyl)amino) propan-2-yl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DGGDA-DOPO)

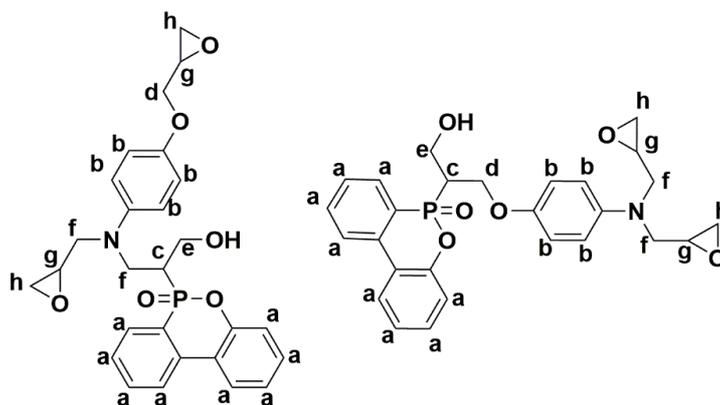


Figure 1: DGGDA-DOPO structure

In a 500 mL three-necked round-bottom flask equipped with a condenser and a mechanical stirrer, 100 g (0.361 mol, 1 eq.) of DGGDA and 77.89 g (0.361 mol, 1 eq.) of DOPO were introduced and purged with N<sub>2</sub> during 30 min. Then, the reaction mixture was allowed to heat at 155 °C for 6h. At the end, the reaction was frozen and ground to obtain a pale-yellow powder of DGGDA-DOPO (Figure 1) with 98 % yield. The phosphorus ratio was 6.3 wt% in this product and the EEW was 2.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, ppm): δ = 2.57 (m, 2H, H<sub>h</sub>), 2.74 (m, 2H, H<sub>h</sub>), 2.88 (t, 2H, H<sub>g</sub>), 3.15 (m, 2H, H<sub>d</sub>), 3.35 (m, 2H, H<sub>f</sub>), 3.67 (td, 2H, H<sub>f</sub>), 3.91 (m, 1H, H<sub>e</sub>), 4.16 (dd, 1H, H<sub>c</sub>), 6.45-6.9 (m, 4H, H<sub>b</sub>), 7.09-8.20 (m, 8H, H<sub>a</sub>). (Figure SI 1)

<sup>31</sup>P NMR (161.6 MHz, DMSO-d<sub>6</sub>, ppm): δ 36.79 ppm. (Figure SI 2)

HRMS (ESI+): calc. for [M + H<sup>+</sup>] 494.17 g.mol<sup>-1</sup>, found 494.17 g.mol<sup>-1</sup>.

Niklasson *et al.* have studied the impact of heteroatoms in the structure of phenyl glycidyl ether.<sup>34</sup> Their study has demonstrated that heteroatoms such as oxygen and nitrogen have a similar reactivity. Those results allowed to conclude that there is a mixture of the two structures presented in Figure 1.

**Synthesis of 4-((4-((3-hydroxy-2-(6-oxidodibenzo[*c,e*][1,2]oxaphosphinin-6-yl)propyl)((2-oxo-1,3-dioxolan-4-yl)methyl)amino)phenoxy)methyl)-1,3-dioxolan-2-one (DGGDAC-DOPO)**

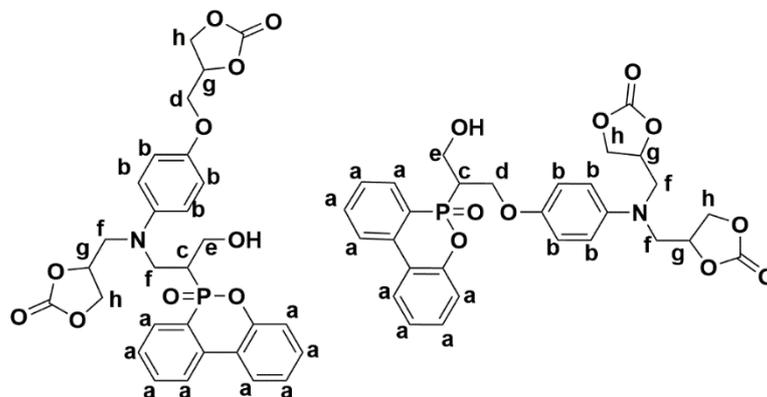


Figure 2: DGGDAC-DOPO structure

DGGDA-DOPO (200 g, 0.405 mol) and tetrabutylammonium bromide (3.919 g, 0.012 mmol) were solubilized in 200 mL of dichloromethane (DCM) and added to a 600 mL sealed reactor. The reaction was carried out at 80 °C under 20 bars of CO<sub>2</sub> for 120 h. The crude mixture was then washed with water and brine to remove TBAB. The organic layer was then dried with magnesium sulfate and under vacuum. The pure product, presented in Figure 2, was obtained as a yellowish viscous liquid with a 78 % yield. The phosphorus ratio was 5.3 wt% in this product and the CEW was 2.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ = 2.69 (m, 2H, H<sub>d</sub>), 3.35-3.75 (m, 4H, H<sub>i</sub>), 3.80-3.91 (m, 2H, H<sub>e</sub>), 4.04-4.24 (m, 4H, H<sub>n</sub>), 4.38 (m, 1H, H<sub>c</sub>), 4.55-4.68 (m, 2H, H<sub>g</sub>), 4.85 (s, 1H, OH), 5.12 (s, 1H, OH), 6.45-6.93 (m, 4H, H<sub>b</sub>), 7.20-8.27 (m, 8H, H<sub>a</sub>). (Figure SI 3)

<sup>31</sup>P NMR (161.6 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 36.79 ppm. (Figure SI 4)

HRMS (ESI+): calc. for [M + H<sup>+</sup>] 582.15 g.mol<sup>-1</sup>, found 582.15 g.mol<sup>-1</sup>

Experimental phosphorus content: 5.98 % wt P

**Synthesis of DGGDAC-DOPO-MXDA oligomer**

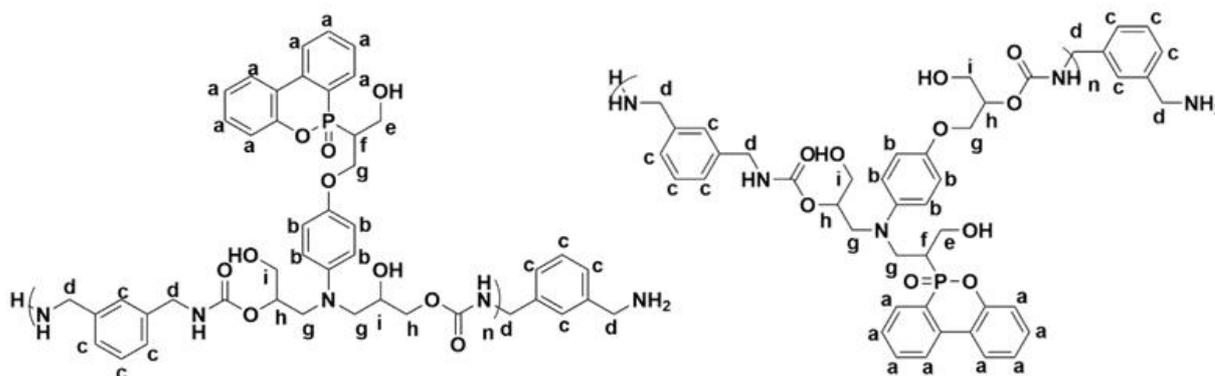


Figure 3: DGGDAC-DOPO-MXDA oligomer structure

DGGDAC-DOPO (50 g, 0.086 mol, 2 eq.) and MXDA (17.6 g, 0.129 mol, 3 eq.) were added in a 250 mL round bottom flask equipped with a mechanical stirrer and 100 mL of DCM. The mixture was stirred 15 h at 35 °C. At the end of the reaction, the solvent was removed under reduced pressure (10 mbar) at 30 °C, and a pale orange powder was obtained. The DGGDAC-DOPO-MXDA oligomer exhibits a phosphorus content of 4.2 wt% and the structure is presented in Figure 3.

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ , ppm):  $\delta$  = 3.17 (m, 4H, H<sub>i</sub>), 3.43 (m, 4H, H<sub>h</sub>), 3.57 (m, 6H, H<sub>g</sub>), 3.84 (s, 4H, H<sub>d</sub>) 4.00 (m, 1H, H<sub>f</sub>), 4.19 (m, 2H, H<sub>e</sub>), 4.45-5.37 (m, 3H, OH), 6.45-6.93 (m, 4H, H<sub>b</sub>), 7.23-7.43 (m, 4H, H<sub>c</sub>), 7.20-8.27 (m, 8H, H<sub>a</sub>). (Figure SI 5)

$^{31}\text{P}$  NMR (161.6 MHz, DMSO- $d_6$ , ppm):  $\delta$  36.79 ppm. (Figure SI 6)

Experimental phosphorus content: 3.94% wt P

### Synthesis of DGGDAC-DOPO-MXDA containing alkyd resins

In order to prepare phosphorylated PAHU resins, the previously synthesized DGGDAC-DOPO-MBDAC oligomer was reacted, in different ratios with a commercial alkyd resin, having excess acid functions, kindly supplied by Lixol. This AR exhibited an acid value (AV) of 55 mg KOH.g<sup>-1</sup>. It is defined as the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of alkyd resin and it represents the free acid groups in the resins. Alkyd resin, DGGDAC-DOPO-MXDA and *p*-toluenesulfonic acid (*p*TSA) were added in a five-necked reactor flask equipped with a mechanical stirrer, a condenser, a thermometer and a nitrogen inlet. The reaction was carried out at temperatures between 160-170 °C under nitrogen atmosphere. Table 1 summarized the different amounts of alkyd resins and PHU oligomer introduced in the reactor. The reference alkyd resin was mixed during 5 hours at 160-170 °C with 2 wt% of *p*TSA to ensure that it did not react on itself. Then, for DGGDAC-DOPO-MXDA containing alkyd resins, samples of the reaction mixture were periodically taken out and were monitored by applying a drop of sample on a clean glass plate and then observing their clarity after evaporating the solvent. The reaction was carried out until a homogenous drop was obtained. The progress of the reaction was also monitored by the AV. The decrease of AV indicates that functions react and corresponds to advancement of step growth polymerization. Final ARs contained 20 wt% of solvent, 1-methoxy-2-propanol.

Table 1: Amounts of the reagents for the synthesis of phosphorylated PAHU resins

	Theoretical Wt %P	Alkyd resin (N.V.C.) (wt %)	DGGDAC- DOPO-MXDA (wt %)	<i>p</i> TSA (wt %)
Reference	0	100	0	2
PAHU 0.5	0.5	88	12	2
PAHU 1	1	76	24	2
PAHU 1.5	1.5	64	36	2

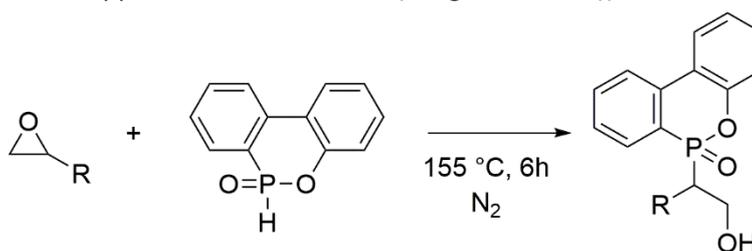
## 3. Results and discussion

### a) Synthesis

#### Synthesis of DGGDA-DOPO

The synthesis of DGGDA-DOPO monomer is presented in Scheme 2. DOPO and DGGDA monomers were added in stoichiometric ratio 1:1, in order to obtain only one DOPO per monomer and keep at least two epoxy functions able to react during the synthesis of a linear oligomer. The reaction was stirred at 155 °C for 6 h. The synthesis was based on nucleophilic attack of the P<sup>-</sup> of the DOPO, obtained at high temperature, onto the epoxide group.<sup>30</sup> This nucleophilic attack allowed the opening of the oxirane group and the formation a P-C bond and a hydroxyl group. Moreover, the nucleophilic attack occurred on the less substituted carbon of the epoxide leading to the corresponding  $\beta$ -hydroxyphosphinate. The formation of P-C bond was investigated by  $^{31}\text{P}$  NMR. Indeed, the disappearance of the chemical shift at 16 ppm for DOPO and the appearance of the

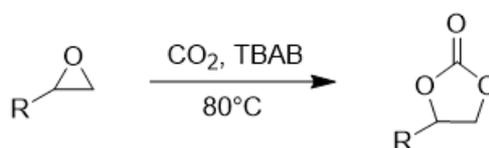
chemical shift at 36 ppm are characteristic of the formation of a P-C bond. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra are presented in supplemental information (SI figure 1 and 2)).



Scheme 2: Synthesis of phosphorus flame retardant DGGDA-DOPO

The  $^1\text{H}$  NMR was used to determine the epoxy equivalent weight (EEW) of epoxy-DOPO monomers and to compare it with the EEW of the epoxy before the synthesis. The value of EEW of DGGDA and MBDA was  $3 \text{ g}\cdot\text{eq}^{-1}$  before the synthesis with DOPO. After the synthesis, the value decreased to  $2 \text{ g}\cdot\text{eq}^{-1}$  which confirmed that only one epoxy group per molecule in average has reacted with DOPO.

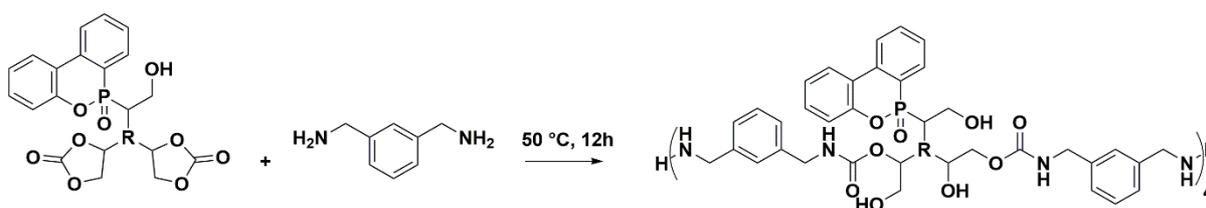
### Synthesis of DGGDAC-DOPO



Scheme 3: Synthesis of carbonate DGGDAC-DOPO

The DGGDA-DOPO obtained during the previous step was carbonated to obtain cyclocarbonates as presented in Scheme 3. Such reaction is carried out in pressurized reactor containing phase transfer catalyst (TBAB), 20 bars of  $\text{CO}_2$  in dichloromethane.<sup>35</sup> After 120 h at  $80 \text{ }^\circ\text{C}$  the reaction was stopped and the TBAB was removed by liquid-liquid extraction. The dried products were characterized by  $^1\text{H}$  and  $^{31}\text{P}$  NMR and FTIR (NMR SI figure 3 and 4). A value of CEW of  $2 \text{ g}/\text{eq}$  was calculated based of the  $^1\text{H}$  NMR analysis of the product.

### Synthesis of DGGDAC-DOPO-MXDA oligomer



Scheme 4: Synthesis of DGGDAC-DOPO-MXDA oligomer

The synthesis of PHU oligomer was obtained by reacting DGGDAC-DOPO with an excess of an aromatic diamine (MXDA). The excess of diamine allows to functionalize oligomers by terminal amine groups able to react with excess acid functions of alkyd resin and leading to the formation of amide functions. Thanks to Flory's theory and Carothers' equation, a ratio diamine:cyclocarbonate of 3:1 allowed to determine a degree of polymerization of 5. The oligomer was characterized by  $^1\text{H}$  and  $^{31}\text{P}$  NMR, FTIR and SEC analyses.

The FTIR analysis of the DGGDAC-DOPO-MXDA oligomer showed the complete transformation of the  $\text{C}=\text{O}$  ( $1787 \text{ cm}^{-1}$ ) from the cyclic carbonate into  $\text{C}=\text{O}$  of urethane at  $1699 \text{ cm}^{-1}$  (Figure 4).

The PHU oligomer exhibited a molar mass of the repetitive unit of  $718 \text{ g}\cdot\text{mol}^{-1}$ . The results from the SEC analyses showed that the number-average molar mass of DGGDAC-DOPO-MXDA oligomer was

2,800 g.mol<sup>-1</sup> with a dispersity ( $\bar{M}_w/\bar{M}_n$ ) of 1.6. These results assumed that the average degree of polymerization ( $n$ ) was equal to 4 which is not exactly the same with the theoretical degree of polymerization calculated with Carothers' equation but consistent.

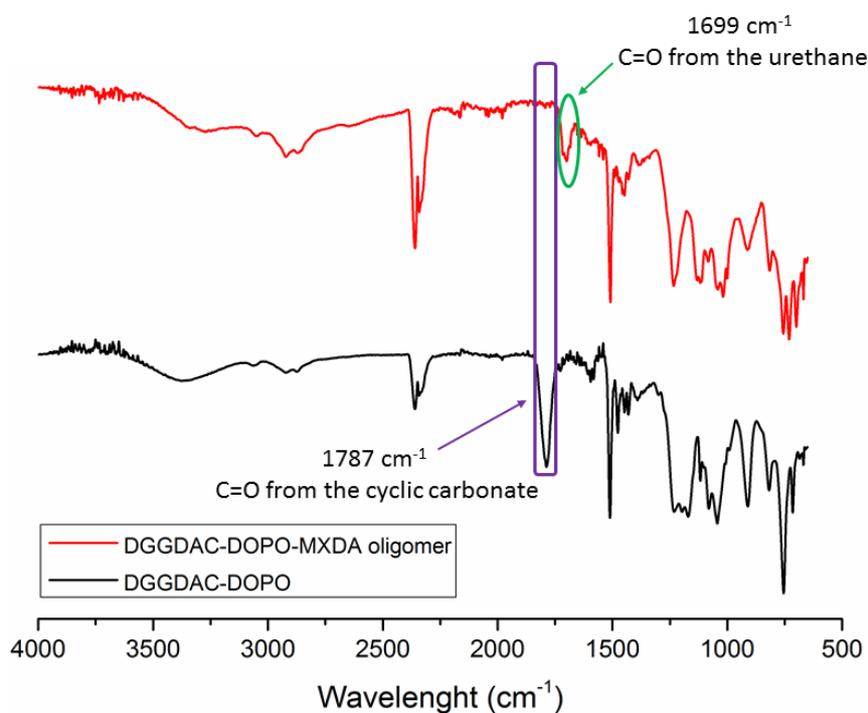


Figure 4: FTIR analyses of DGGDAC-DOPO and DGGDAC-DOPO-MXDA oligomer

### Synthesis of phosphorylated PAHU resins

As the beginning of the reaction, the mixture was heterogeneous due to the immiscibility between the alkyd resin and the PHU oligomer. Then, the progress of the reaction was monitored by taking sample periodically and depositing a drop of the reaction mixture on a glass plate. The presence of orange grainy particles inside the drop indicated that a part of DGGDAC-DOPO-MXDA oligomer was unreacted. The reaction was carried out until a homogenous drop was obtained. Moreover, the decrease of acid value was also another indication of the progress of the reaction. However, the bond between the oligomer and the alkyd resins was determined by <sup>1</sup>H DOSY NMR (Figure 5). DOSY NMR is used to determine the self-diffusion coefficients of molecules in a solution. All the spots belonging to the same polymer are aligned and exhibit the same diffusion coefficient. Indeed, the aromatic characteristic peak of the MXDA contained in the DGGDAC-DOPO-MXDA oligomer at 6.8 ppm exhibited the same diffusion coefficient as the alkyd resin, at  $-10.5 \log (\text{m}^2 \cdot \text{s}^{-1})$ . Thus, it confirmed the covalent bond between the two polymers. Side-reactions such as cyclization also occurred during the polymerization of the alkyd resins leading to cycles with low molar masses.<sup>36,37</sup> Thus the diffusion coefficient of those cycles exhibited a different value at  $-9.3 \log (\text{m}^2 \cdot \text{s}^{-1})$ . This phenomenon is not controlled and appears at any time during polycondensation. DOSY NMR of the others alkyd resins are provided in SI Figures 7 and 8 and showed the same result as the DOSY NMR for PAHU 1 wt% P.

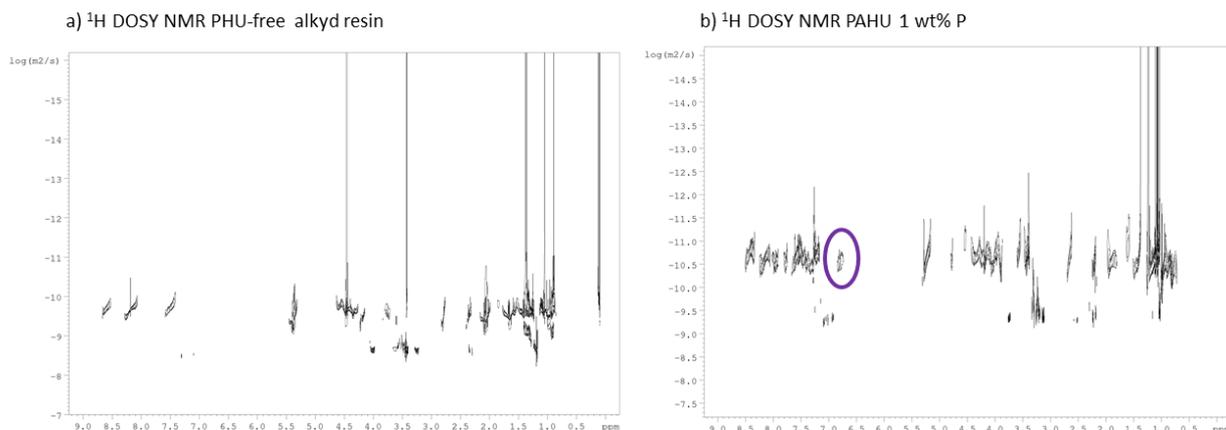


Figure 5:  $^1\text{H}$  DOSY NMR of a) PHU-free alkyd resin and b) PAHU 1 wt% P resin

Moreover, the evolution of the acid value was also monitored and a decrease indicated that acid functions reacted with amines or hydroxyl functions of PHU oligomer. Theoretically, in view of the higher steric hindrance around the hydroxyl functions, the amine functions should react preferentially with acid functions, leading to the formation of amide functions. To confirm this assumption, FTIR analysis was performed (Figure 6) and demonstrated a disappearance of the peak corresponding to the amine functions at  $1540\text{ cm}^{-1}$  in the PAHU resins with 0.5, 1 and 1.5 wt% P. This result confirmed the formation of covalent bonds between the PHU oligomer and the alkyd resin through the reaction between hydroxyl and amines functions, leading to amide groups. Nevertheless, the characteristic peak of the C=O of amide functions and the C=O of ester and urethane functions have close vibration frequencies. Thus, monitoring the progress of the reaction in FTIR is not possible so only the visual analysis allowed the evolution of grafting.

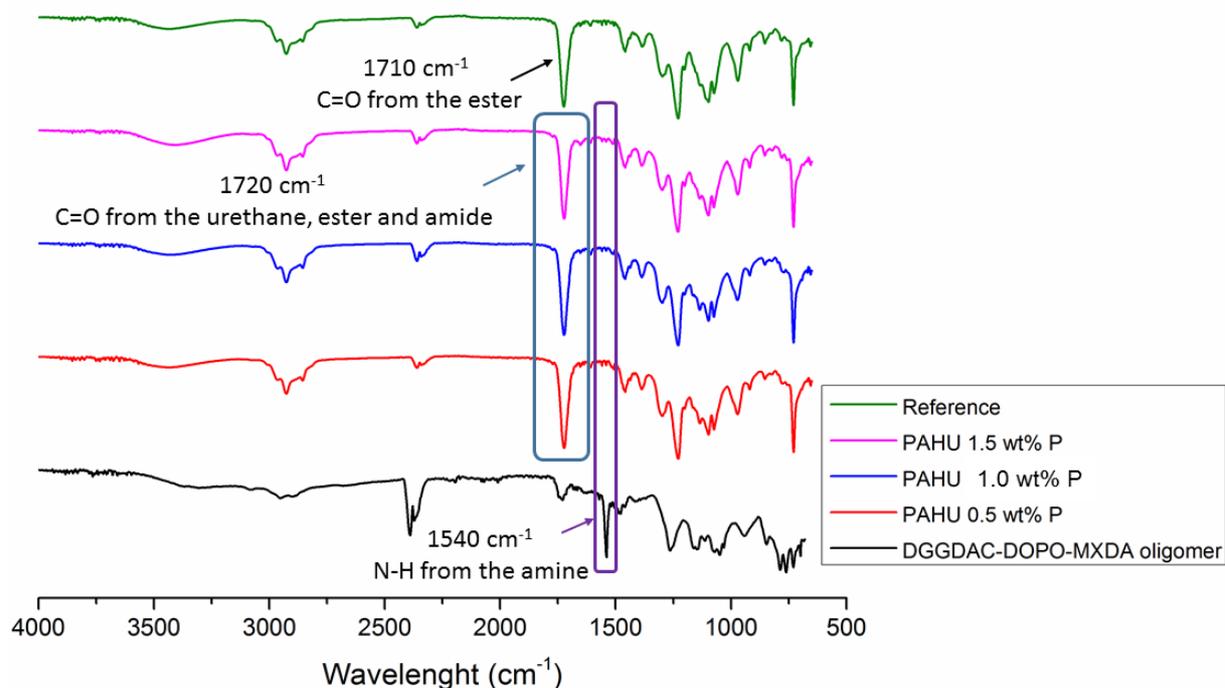


Figure 6: FTIR analyses of PHU oligomer, reference alkyd resin and PAHU resins

The final acid values, hydroxyl values and oil lengths of PAHU resins are presented in Table 2. As expected, the final content of fatty acids in the composition of alkyd resins decreased due to the increasing amount of PHU oligomer incorporated. Thereby, all the final alkyd resins exhibited between 37 and 55 wt% of fatty acids in their composition, so they could be classified as medium oil length. It is defined as the mass percentage of fatty chains on the total mass of the alkyd resin. Final acid value decreased and final hydroxyl value increased with the increasing amount of DGGDAC-DOPO-MXDA oligomer. Indeed, the more PHU oligomer is introduced, the more hydroxyl functions are introduced in the reaction and the more amine functions react with acid functions. The phosphorus content was confirmed by elementary analysis on the alkyd hybrid resins and they are close to the theoretical weight content (Table 2 and SI-part 2).

Table 2: Final acid and hydroxyl values and final oil length of PAHU alkyd resins

	Theoretical Wt %P	Experimental Wt % P*	Acid value before reaction (mol)	$f_{NH_2}$ (mol)	Final acid value (mol)	Final acid value (mg.KOH <sup>-1</sup> )	Final hydroxyl value	Final oil length (%)
Reference	<b>0.0</b>	<b>0</b>	<b>0.123</b>	<b>0.000</b>	<b>0.123</b>	<b>55</b>	<b>0.000</b>	<b>55</b>
PAHU 0.5	<b>0.5</b>	<b>0.52</b>	<b>0.108</b>	<b>0.011</b>	<b>0.097</b>	<b>49</b>	<b>0.016</b>	<b>49</b>
PAHU 1	<b>1.0</b>	<b>0.80</b>	<b>0.093</b>	<b>0.021</b>	<b>0.072</b>	<b>42</b>	<b>0.064</b>	<b>43</b>
PAHU 1.5	<b>1.5</b>	<b>NC</b>	<b>0.078</b>	<b>0.032</b>	<b>0.046</b>	<b>32</b>	<b>0.096</b>	<b>37</b>

\*All the details of the results were added in supplementary material (part 2)

#### b) Characterizations of poly(alkyd hydroxyurethane) resins

##### Structural characterizations of the PAHU

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. The results (based on PMMA equivalent) are presented in Table 3. The  $M_w$  of the reference alkyd resin was low and it could be concluded that the reference is an oligomer of alkyd. As expected,  $M_n$  and  $M_w$  values increased with the amount of PHU oligomer introduced. Indeed, the oligomer was grafted as a linker between two alkyd chains which increased the hydrodynamic volume and led to a higher molar mass. Thereby, this increment was another indication of bond formation between the resin and the DGGDAC-DOPO-MXDA oligomer. The  $\mathcal{D}$  was similar for all the alkyd resins.

Table 3:  $M_w$ ,  $M_n$  and  $\mathcal{D}$  results of PAHU resins

	Wt %P	$M_w$ (g.mol <sup>-1</sup> )	$M_n$ (g.mol <sup>-1</sup> )	$\mathcal{D}$
DGGDAC-DOPO- MXDA oligomer	<b>4.2</b>	<b>2 800</b>	<b>1 800</b>	<b>1.6</b>
Reference	<b>0.0</b>	<b>2 000</b>	<b>1 500</b>	<b>1.3</b>
PAHU 0.5	<b>0.5</b>	<b>6 000</b>	<b>3 000</b>	<b>2.0</b>
PAHU 1	<b>1.0</b>	<b>9 000</b>	<b>6 000</b>	<b>1.5</b>
PAHU 1.5	<b>1.5</b>	<b>12 200</b>	<b>6 000</b>	<b>2.0</b>

The gel content (GC) was determined to confirm the presence of a covalent network after drying. Dry films were obtained with the introduction of a catalyst based on metallic salt to accelerate the

autoxidation of alkyd resins. For all the alkyd resins, the GC, presented in Table 4, were higher than 90 %, which confirms total crosslinking of the two polymers.

Differential scanning calorimetry (DSC) analyses were investigated to determine the glass transition temperature ( $T_g$ ), and the results were reported in Table 4. The  $T_g$  values increased with the introduction of DGGDAC-DOPO-MXDA oligomer, which indicated an increase of the rigidity of the material. The PHU-free alkyd resin exhibited a  $T_g$  value of 3 °C while the introduction of DGGDAC-DOPO-MXDA oligomer increased the  $T_g$  values up to 20 °C. This evolution was mainly due to the increase of the molar mass and the introduction of aromatic groups of DOPO, DGGDAC and MXDA. The highest  $T_g$  was obtained with the alkyd resin containing 1.5 wt% P DGGDAC-DOPO-MXDA, as expected. However, all the  $T_g$  were in the same range of values.

Viscometry analyses were performed at 20 °C with a shear rate of 10 s<sup>-1</sup>. All the resins were compared with the same non-volatile content of 80 wt% and the results are presented in Table 4. Hybrid alkyd resins exhibited a higher viscosity than the reference alkyd resin, which was expected since the molar mass of the PHU-free alkyd resin was lower than the DGGDAC-DOPO-MXDA containing alkyd resins. Moreover, the presence of bulky groups, such as phenyl groups of the DGGDAC, DOPO and MXDA increases the viscosity. Furthermore, the viscosity of alkyd resins increased from 5.8 Pa.s for the PHU-free alkyd resin to 11.3 Pa.s with 1.5 wt% of phosphorus. Those results are consistent with those obtained by SEC. However, despite the increase of viscosity, those values are acceptable and the performance of PAHU resins could be maintained as well as the intended application.

Table 4: Viscosity, glass transition temperature and gel content of PAHU resins

	Wt %P	$\eta$ (Pa.s)	$T_g$ (°C)	Gel content* (%)
Reference	<b>0.0</b>	<b>5.8</b>	<b>3</b>	<b>94</b>
PAHU 0.5	<b>0.5</b>	<b>9.2</b>	<b>8</b>	<b>94</b>
PAHU 1	<b>1.0</b>	<b>9.8</b>	<b>14</b>	<b>92</b>
PAHU 1.5	<b>1.5</b>	<b>11.3</b>	<b>20</b>	<b>95</b>

\*after drying at room temperature with 5 wt% catalyst

The formation of amide groups in alkyd resins could improve the thixotropy, a rheological property of the resin. Thixotropy is defined as the continuous decrease of viscosity with time when flow is applied to a sample that has been previously at rest and the subsequent recovery of viscosity in time when the flow is discontinued.<sup>38-42</sup> This phenomenon is generally used to modify the rheological properties of paints. The flow curves ( $\tau = f(\dot{\gamma})$  presented in Figure 7) were obtained by regularly increasing the shear rate from 0.1 to 100 s<sup>-1</sup>, and then decreasing gradually to return to 0.1 s<sup>-1</sup>. A thixotropic sample exhibits a hysteresis loop because the stress lags the shear rate. Thereby, the wider is the hysteresis loop, the more the material exhibits thixotropic properties. The curve  $\tau = f(\dot{\gamma})$  of PHU-free alkyd resin presented in Figure 7, did not show a hysteresis loop, thus the reference alkyd resin did not exhibit thixotropic properties, as expected. The curves of PAHU alkyd resins, which contained amide groups, showed increasingly large loops with the growing amount of DGGDAC-DOPO-MXDA oligomer. The hysteresis loops remained small and providing optimal thixotropic properties would require the formation of additional amide functions. Nevertheless, those results could improve the transfer of the paint to the brush or roller and reduce the tendency of the paint to drip and splatter when applied.

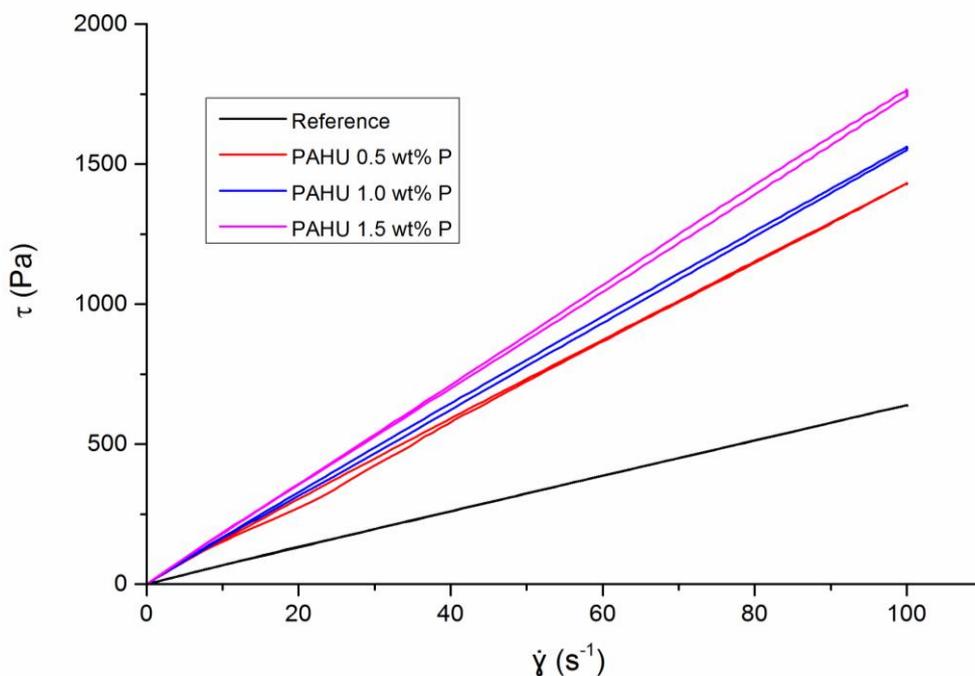


Figure 7: Hysteresis loop of PAHU resins

### Film properties

Dry films with a thickness of 80  $\mu\text{m}$  were obtained 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 5 and Table 6.

Table 5: Adhesion, hardness, gloss, drying time and color of PAHU resins

	Wt %P	Adhesion	Hardness (s)	Gloss 20°/60° (G.U.)	Drying time (min)	Color
Reference	<b>0.0</b>	<b>0</b>	<b>41</b>	<b>80/96</b>	<b>190</b>	<b>5</b>
PAHU 0.5	<b>0.5</b>	<b>0</b>	<b>66</b>	<b>79/94</b>	<b>170</b>	<b>18</b>
PAHU 1	<b>1.0</b>	<b>0</b>	<b>68</b>	<b>72/95</b>	<b>155</b>	<b>18</b>
PAHU 1.5	<b>1.5</b>	<b>0</b>	<b>66</b>	<b>74/98</b>	<b>120</b>	<b>16</b>

All the samples exhibited excellent adhesion properties. Indeed, the edges of the cuts were completely smooth and none of the squares of the grid were torn off. The results allow an evaluation as class 0 according to ISO2409:2020. The introduction of the oligomer DGGDAC-DOPO-MXDA in alkyd resins did not impact the adhesion properties of the resins.

The hardness of the coating was impacted by the amount of PHU oligomer introduced. The more flexible is the film, the faster the pendulum is damped and therefore the less oscillations are required. Indeed, the more flexible is the film, the more it is able to absorb the energy of the pendulum. The number of oscillations increased from 41 for the reference resin to 66 for the PAHU with 1 wt% P. It means that the introduction of PHU oligomer provided harder films. Moreover, the hardness was in the same range for the different quantities of PHU oligomer. Nevertheless, even with increased values of hardness for the PAHU resins, the films remained flexible, allowing the resin to maintain its film-forming properties for applications.

The gloss of the coatings was firstly measured at 60° to determine the gloss level. All the alkyd resins exhibited a high gloss level with values superior to 94 (between 94 and 98). The measurements were then studied at 20°. The reference resin showed a value of 80 and all the PAHU resins exhibited values between 72 and 79. The introduction of PHU oligomer in alkyd resins did not impact the gloss of the resins. Moreover, 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 PHU oligomer darkened the resins a lot (from 5 for the reference to 18 for PAHU resins). This was expected because the oligomer had a brown color. Even if the oligomer darkened the alkyd resins, they could be used as primary in paint formulations.

The introduction of the oligomer DGGDAC-DOPO-MXDA improved the drying time. The drying time was reduced by 1 h for the 1.5 wt% P modified alkyd resins compared to the drying time of reference alkyd resin. This result was expected as the introduction of PHU oligomer increased the  $M_w$ .

Table 7 presents the results of the determination of the chemical resistance of the resins. The higher is the weight loss, the lower is the residual mass percentage and the less resistant is the resin to the solvent. All the PAHU resins exhibited similar chemical resistances with the reference alkyd resin for water, HCl and NaCl solutions. However, the synthesis of PAHU resins improved the chemical resistance of the resins to alkali solution (NaOH 0.1 M). Those results were expected as the urethane bonds are well known to improve the chemical resistance of hybrid alkyd resins.<sup>8,11</sup> This improvement of alkali solution resistance could allow the use of PAHU resins for marine paints or varnishes in environments near the sea.

Table 6: Chemical resistance to acid and alkali solutions of PAHU resins

	Wt %P	Water	HCl (0.1 M)	NaCl (5 %)	NaOH (0.1 M)
Reference	0.0	94 ± 1 %	79 ± 4 %	98 ± 2 %	56 ± 4 %
PAHU 0.5	0.5	95 ± 1 %	80 ± 1 %	97 ± 3 %	92 ± 2 %
PAHU 1	1.0	93 ± 3 %	81 ± 2 %	96 ± 3 %	93 ± 2 %
PAHU 1.5	1.5	93 ± 1 %	79 ± 2 %	98 ± 1 %	94 ± 3 %

### c) Thermal and flame retardant properties

Thermal and flame retardancy properties were investigated in this part to highlight the influence of phosphorylated PHU oligomer in alkyd resins.

#### Thermogravimetric analysis

The thermal properties of all alkyd resin films were investigated by thermogravimetric analyses (TGA) under nitrogen flow. Figure 8 shows the thermograms of the phosphorylated PAHU with, respectively, 0.5 wt%, 1 wt% and 1.5 wt% of phosphorus brought by DGGDAC-DOPO-MXDA oligomer. Thermal properties such as the temperature at 5 % and 50 % weight loss, and the residue yield at 850 °C, are summarized in Table 7. Firstly, the temperature at 5 % weight loss ( $T_{d,5wt\%}$ ) increased with the introduction of DGGDAC-DOPO-MXDA oligomer. Indeed, the  $T_{d,5wt\%}$  was improved, going from 180 °C for the PHU-free alkyd resin to around 230 °C with phosphorus PHU containing alkyd resins. At this temperature, a polycondensation reaction could occur between the remaining hydroxyl and acid functions of the reference alkyd resin, releasing water. This reaction did not occur for the

phosphorus containing alkyd resins because the remaining acid functions of alkyd resins had been previously reacted with the amine functions of DGGDAC-DOPO-MXDA oligomer leading to the formation of phosphorylated PAHU. Then, considering the temperature at 50 % weight loss ( $T_{d,50wt\%}$ ) the thermal stability exhibited values between 440 and 430 °C for all the alkyd resins. The residue yield was increased, up to 16.5 % with 1.5 wt% P. The residue yield was promoted by the aromatic rings in the structure of DGGDAC-DOPO-MXDA oligomer and by the catalytic action of phosphorus groups even if DOPO is not believed to be an efficient char promoter<sup>43-44</sup> (contrarily to phosphate or phosphonated-based FR).

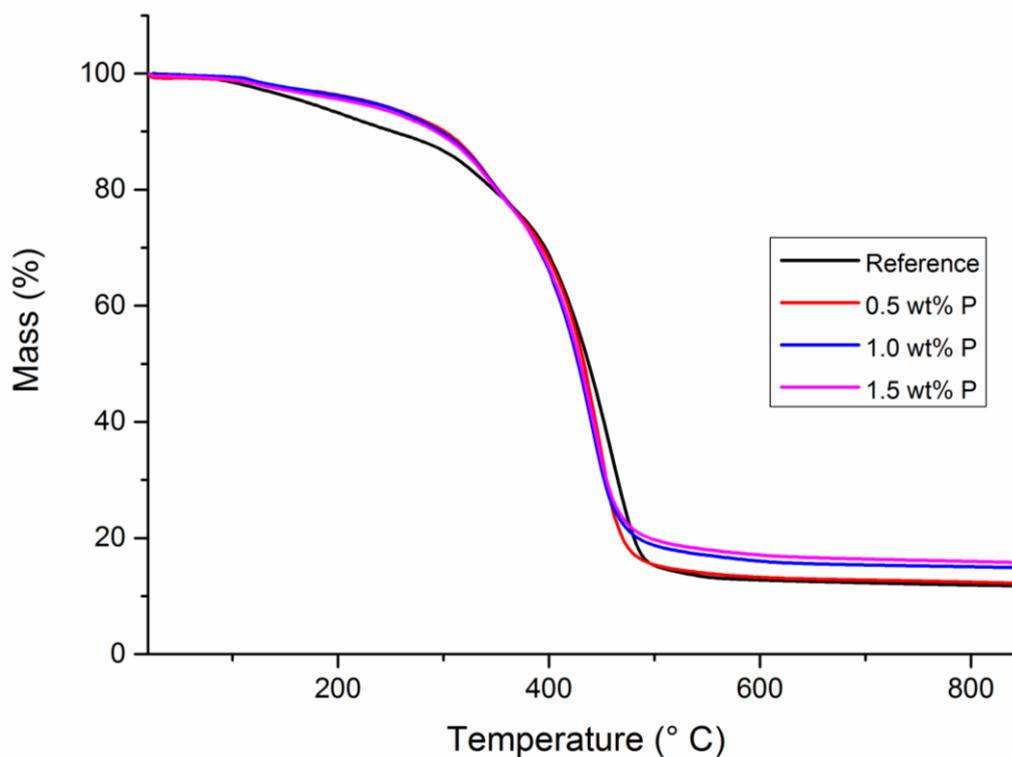


Figure 8: TGA curves of PAHU resins

Table 7: TGA results of PAHU resins

	Wt %P	$T_{d,5\%}$ (°C)	$T_{d,50\%}$ (°C)	Residue at 850 °C
Reference	<b>0.0</b>	<b>180</b>	<b>440</b>	<b>10.0</b>
PAHU 0.5	<b>0.5</b>	<b>233</b>	<b>433</b>	<b>12.0</b>
PAHU 1	<b>1.0</b>	<b>231</b>	<b>430</b>	<b>14.5</b>
PAHU 1.5	<b>1.5</b>	<b>230</b>	<b>429</b>	<b>16.5</b>

### Pyrolysis combustion flow calorimeter analysis

Table 8 summarizes the data obtained from PCFC analyses. 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 9 exhibits the

PCFC curves of the PAHU resins. The increased amount of DGGDAC-DOPO-MXDA oligomer provided a reduction in pHRR and THR values which demonstrated the FR properties of this phosphorylated oligomer. The pHRR of the PHU-free alkyd resin exhibited values of  $244 \text{ W.g}^{-1}$  whereas the pHRR were  $194 \text{ W.g}^{-1}$ ,  $180 \text{ W.g}^{-1}$  and  $160 \text{ W.g}^{-1}$  for the PAHU resins with 0.5 wt% P, 1 wt% P and 1.5 wt% P, respectively. The small peak at low temperature (300-350 °C) is also reduced in presence of PHU. The increasing amount of phosphorus provided better thermal stability, which is consistent with the TGA results. The temperature of the pHRR slightly decreased with the introduction of DGGDAC-DOPO-MXDA oligomer. Nevertheless, all the alkyd resins exhibited a temperature of the pHRR between 435 and 455 °C which is also consistent with TGA results. THR values decreased with increasing amounts of phosphorus in alkyd resins. Indeed, the THR value was decreased from  $21.9 \text{ KJ.g}^{-1}$  for the PHU-free alkyd resin to  $14.6 \text{ KJ.g}^{-1}$  for the alkyd resins with 1.5 wt% P. The energy of complete combustion ( $\Delta h$ ) slightly decreased with the amount of phosphorylated PHU oligomer. Furthermore, the residual content increased from 5 % to 25 % with 1.5 wt% P of DGGDAC-DOPO-MXDA oligomer. These increases demonstrated that oligomer promoted char formation. This could be due to the high content of aromatic rings in the oligomer structure.

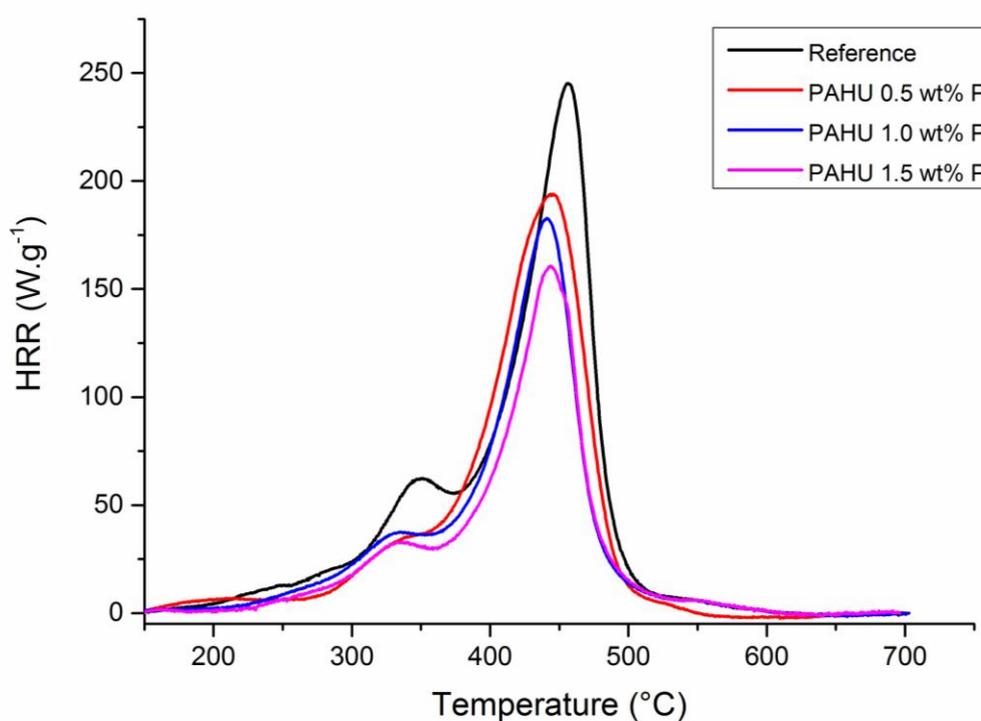


Figure 9: PCFC curves of PAHU resins

Table 8: PCFC results of PAHU resins

	Wt %P	pHRR ( $\text{W.g}^{-1}$ )	T at pHRR (°C)	THR ( $\text{KJ.g}^{-1}$ )	Residue content (%)	$\Delta h$ ( $\text{KJ.g}^{-1}$ )
Reference	<b>0.0</b>	<b>244</b>	<b>455</b>	<b>21.9</b>	<b>5</b>	<b>23.1</b>
PAHU 0.5	<b>0.5</b>	<b>194</b>	<b>444</b>	<b>18.2</b>	<b>12</b>	<b>20.7</b>
PAHU 1	<b>1.0</b>	<b>180</b>	<b>440</b>	<b>16.1</b>	<b>18</b>	<b>19.6</b>
PAHU 1.5	<b>1.5</b>	<b>160</b>	<b>435</b>	<b>14.6</b>	<b>25</b>	<b>19.4</b>

### Cone calorimeter

The cone calorimeter analyses provide important information on the fire behavior of a material.<sup>45</sup> Cone calorimeter tests were performed with a heat flux of  $35 \text{ kW.m}^{-2}$  under ventilated conditions. The results are summarized in Table 9, and Figure 10 exhibits the cone calorimeter curves. Tests were performed on wood samples with 1 g of dry resin as a coating. The curves present two pHRR which is very common with wood samples. The first peak represents the heat release rate (pHRR<sub>1</sub>) reached just after the ignition. After this first 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. 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 (pHRR<sub>2</sub>). This second peak of heat release rate is induced by the wood and its thickness and density, and is independent on the coating. All the samples have a wood thickness of around  $25 \pm 0.2 \text{ mm}$ .

Wood without coating presented a moderate pHRR<sub>1</sub> at  $190 \text{ kW.m}^{-2}$  and the reference alkyd resin led to a strong enhancement of the pHRR<sub>1</sub> up to  $330 \text{ kW.m}^{-2}$ . 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. The objective was to provide a coating with better flame retardancy than a standard coating. The introduction of DGGDAC-DOPO-MXDA oligomer had a strong influence on the pHRR<sub>1</sub>. This must be assigned to its action in condensed phase (by modifying decomposition pathway and promoting char) and maybe also in gas phase (DOPO is well known as flame poisoner, but it is not possible to prove this mode-of-action in this study, while the negligible amount of paint cannot modify significantly the combustion efficiency).<sup>46</sup> Indeed, pHRR<sub>1</sub> decreased with the growing amount of DGGDAC-DOPO-MXDA in alkyd resins. The lowest pHRR<sub>1</sub> was obtained with 1.5 wt% P in the matrix polymer. Indeed, the introduction of up to 1.5 wt% P has improved flame retardancy by decreasing the pHRR<sub>1</sub> from  $330 \text{ kW.m}^{-2}$  to  $176 \text{ kW.m}^{-2}$  which corresponds to a decrease by almost 50 % compared to the FR-PHU-free alkyd resin.

Time to ignition (TTI) measures the time to achieve sustained flaming combustion at a particular external heat flux. TTI was doubled with the introduction of 0.5 wt% P of DGGDAC-DOPO-MXDA oligomer. The longest time to ignition was obtained with 1.5 wt% P with a value of 90 s, which is three times higher than the TTI of the FR-PHU-free alkyd resin and even higher than the TTI of uncoated wood.

The total heat release (THR) of alkyd resins may slightly decrease with increasing amounts of PHU oligomer from  $10.1 \text{ MJ.kg}^{-1}$  for the reference alkyd resin to  $9.1 \text{ MJ.kg}^{-1}$  for the PAHU with 1.5 wt% P. Nevertheless, the presence of a coating was not significant on the THR which was measured during the whole analysis and not only for the pHRR<sub>1</sub>, whereas the coating only had an effect on pHRR<sub>1</sub>.

All those results confirmed the benefits of phosphorus PHU oligomer on flame retardant properties.

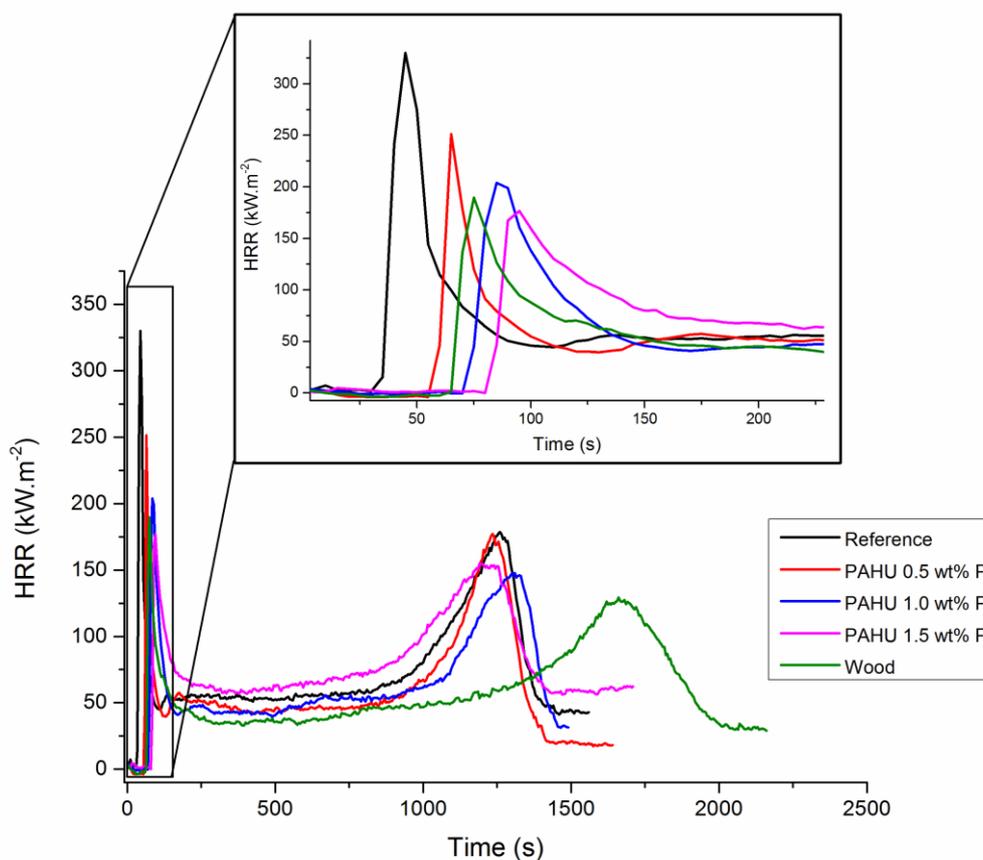


Figure 10: Cone calorimeter results of PAHU resins

Table 9: Cone calorimeter results of PAHU resins

	Wt %P	TTI	pHRR (kW.m <sup>-2</sup> )	THR (MJ.g <sup>-1</sup> )
Wood	<b>0.0</b>	<b>65</b>	<b>190</b>	<b>9.4</b>
Reference	<b>0.0</b>	<b>35</b>	<b>330</b>	<b>10.1</b>
PAHU 0.5	<b>0.5</b>	<b>60</b>	<b>255</b>	<b>9.5</b>
PAHU 1	<b>1.0</b>	<b>80</b>	<b>203</b>	<b>8.8</b>
PAHU 1.5	<b>1.5</b>	<b>90</b>	<b>176</b>	<b>9.1</b>

#### 4. Conclusion

New phosphorylated polyhydroxyurethane oligomers have been successfully synthesized and covalently grafted to alkyd resins. The formation of covalent bonds has been investigated by DOSY NMR. Then, the obtained PAHU hybrid resins have demonstrated an improvement of alkali resistance as well as hardness, compared to reference alkyd resin. Nevertheless, the color was negatively impacted by the introduction of PHU oligomer. In addition, the good adhesion and chemical resistance of PAHU resins as well as the improvement of the hardness allow to formulate primers. Indeed, these formulations are the first layer to be applied on a support before proceeding to its finishing and the color does not matter. Moreover, the improvement of alkali solution resistance could allow the use of PAHU resins in environments near the sea. The fire behavior of those polymers has been investigated by TGA, PCFC and cone calorimeter. All the alkyd resins exhibited better

thermal behavior with phosphorylated PHU oligomer. It has been demonstrated that the PAHU with 1.5 wt% P provided better thermal resistance and flame retardancy. Nevertheless, the results obtained for the PAHU resin with 1.0 wt% P exhibited similar results than the PAHU with 1.5 wt% P. The residue was also favored with the amount of phosphorylated PHU. The introduction of 1.0 wt% P is enough to achieve the desired performance and take into account the commercial cost of this modification. Wood protected with a coating containing 1.0 wt% P exhibited a 40 % reduction in pHRR compared to the reference alkyd resin. The formation of amide bonds provided thixotropy, a new rheological performance of alkyd resins with flame retardants and alkali resistance which could be interesting for paint applications.

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