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Synergistic effect of DOPO and VMDMS for flame retardancy of alkyd resins.

Maxinne Denis^{a,b}, Damien Le Borgne^b, Rodolphe Sonnier^c, Sylvain Caillol^a, Claire Negrell^{a*}

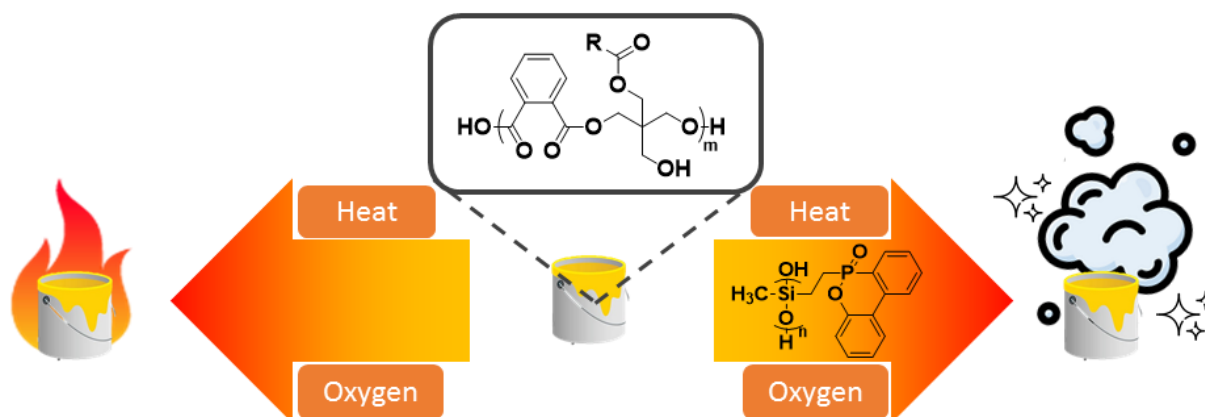
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Graphical abstract



Abstract

New polysiloxane oligomers containing phosphorus, 6-(2-(dihydroxy(methyl)silyl)ethyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-VMDMS), have been synthesized and grafted to the remaining hydroxyl groups of alkyd resins in order to obtain hybrid alkyd resins with flame retardant properties. These silicone alkyd resins have demonstrated better drying time, gloss and chemical resistance than reference alkyd resins without DOPO-VMDMS. Moreover, the thermal and flame retardancy properties have been investigated using differential scanning calorimeter, thermogravimetric analysis and pyrolysis-combustion flow calorimeter. The alkyd resins were applied as a coating on wood and fire behavior was tested by cone calorimeter analysis. The most effective coating contains 30 wt% DOPO-VMDMS and exhibited a 55 % reduction in pHRR compare to the resins without DOPO-VMDMS.

Keywords

Flame retardant; alkyd resin ; DOPO ; silicone ; coating; phosphorous

1. Introduction

Alkyd resins (AR) were developed in the mid-1920s and have since been widely used as binders in paint formulations for the coating industry from the 1930s¹⁻³. The raw materials used for their synthesis are mostly based on renewable resources, which is of great interest due to the current rise in environmental concerns^{2,4}. However, alkyd resins are easily flammable due to their high carbon and hydrogen contents. Therefore, flame retardant

additives (FR) are commonly incorporated into AR to reduce the risk associated with their flammability. The most commercially available flame retardants are halogen-containing compounds, more particularly brominated substances⁵. However, their combustion releases corrosive fumes that are toxic to the environment and human health⁶. Consequently, their use is limited by European regulations and more environmentally alternatives must be developed. Therefore, halogen-free flame retardants have attracted increasing attention in recent years.

Silicone-based compounds are known for their thermal stability without the release of toxic fumes^{7,8} and are considered among the “environmentally friendly” flame retardants. Silica particles have already been used as flame retardants in AR⁹. Indeed, FR containing siloxanes, rearrange themselves into a network of silicone oxide during combustion and provide a thermal protective layer to the polymer residue. In combination with another heteroatom such as phosphorus or nitrogen they can provide a synergistic effect^{10,11}. Moreover, since silicone acts in the condensed phase, its association with a heteroatom which acts mainly in the gas phase is advantageous.

Organophosphorus compounds have been studied for their flame retardant properties in numerous research works over the past few years^{12,13}. Hence, organophosphorus compounds and particularly phosphinates, such as 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), are promising molecules providing this mode of action. Furthermore, these FR are favorable compounds that could replace organohalogen flame retardants^{14,15}.

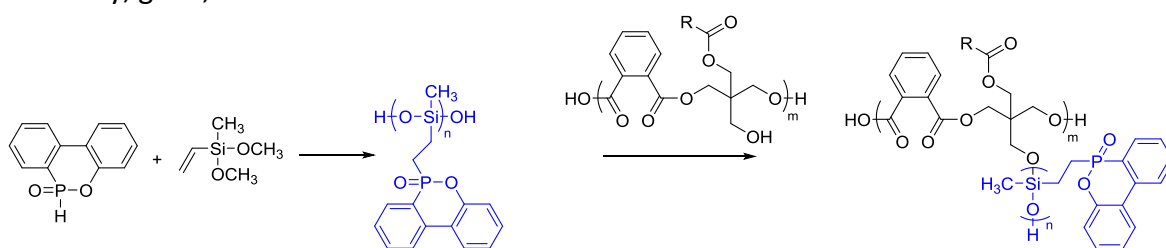
It has been demonstrated that migration and leaching of FR additives are observed after exposure of resins to high temperature or humid atmosphere. To avoid this drawback, reactive additives can be used to create covalent bonds between the polymer matrix and the FR¹³. This method requires a FR with a function able to react with either the co-monomers during polymerization or the polymer thereof. In the case of alkyd resins, carboxyl or hydroxy functions allow copolymerization or grafting.

DOPO is a cyclic phosphinate that has been already reported in the literature due to its attractive properties^{16–20}. Indeed, DOPO exhibits high thermal stability, good resistance to oxidation and water. Moreover, thanks to its reactive P-H bond, DOPO can easily react with unsaturated bonds²¹. Therefore, many DOPO derivatives have been synthesized and found applications in polyurethanes²², polyamides^{23,24}, polyesters^{16,19,25} and epoxy resins^{26–29}. Zhong *et al.* functionalized DOPO with vinylmethyldimethoxy silane (VMDMS) prior grafting onto an oligosiloxane³⁰. The obtained FR was incorporated into a polycarbonate/acrylonitrile butadiene styrene (PC/ABS) blend. The authors highlighted the improvement of flame retardancy as well as the residue content with increasing amounts of FR³⁰. Wang *et al.* also reacted DOPO-VMDMS with bispirocyclic pentaerythritol phosphate to obtain a novel FR additive, which was blended with an ethylene vinyl-acetate copolymer to obtain composites with FR properties⁸. The results of this study demonstrated good flame retardancy with a high char content. Qian *et al.* used a new silicon-containing DOPO compound in the formulation of epoxy resins³¹. The results have demonstrated an increase in char content and an improvement of flame retardant properties. Indeed, the presence of organophosphorus-modified oligosiloxane enhanced the formation of a silicon-rich char which acts as an effective heat shield. Recently, Zhao *et al.* have demonstrated the flame

retardant performance of a polysiloxane coating containing DOPO, used for expandable polystyrene foams³². This FR exhibited excellent flame retardancy with a UL-94 V0 rating, a high limiting oxygen index (36 %), and a low peak of heat release rate (pHRR).

However, to the best of our knowledge, DOPO-VMDMS has never been grafted onto a polymer in order to improve its flame retardancy properties. Moreover, reactive FRs containing silicone and phosphorus have never been reported in alkyd resins. Furthermore, the condensation of siloxane compounds on the remaining hydroxy groups of alkyd resins leads to the formation of hybrid resins^{33–35} which could lead to interesting properties. Hence, a recent review on this topic has demonstrated that the formation of silicone-modified alkyd resins improved outdoor weatherability such as water repellency and resistance to UV-degradation³⁶. The thermal resistance of silicone-based resins has already been studied in the literature. Indeed, some authors reported the use of a blend between alkyd resins and a polysiloxane or SiO₂ nanoparticles^{37–39} in order to improve the thermal stability. Other studies have shown that the decomposition temperature of alkyd resins increased with increasing amounts of grafted silicone compound and led to better durability thanks to the formation of covalent bonds^{33,40,41}. Nevertheless, according to a critical review of the literature, it appears that there is no study on the flame retardant properties of silicone grafted onto alkyd resins with a potential synergistic effect due to heteroatoms such as phosphorus.

In this work, an environmentally friendly flame retardant oligomer containing phosphorus and silicone was synthesized. Then, the resulting oligomer was grafted onto a previously synthesized alkyd resin as shown in Scheme 1. Resins with different amounts of DOPO-VMDMS have been synthesized. Molecular structures and thermal stabilities of the phosphosilanol alkyd resins were characterized by different analyses such as nuclear magnetic resonance (NMR), Fourier Transform Infrared spectroscopy (FTIR), size exclusion chromatography (SEC), thermogravimetric analysis (TGA), pyrolysis combustion flow calorimeter analysis (PCFC) and cone calorimeter. Moreover, film properties such as flexibility, gloss, adhesion and chemical resistance were also studied.



Scheme 1: General synthesis of the hybrid alkyd resin with DOPO-VMDMS oligomer

2. Experimental

2.1. Materials

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was acquired from TCI. Tall oil fatty acid (TOFA), pentaerythritol, phthalic anhydride, maleic anhydride, white spirit, mix of driers (a solution containing cobalt octoate, calcium octoate and zirconium octoate) were kindly supplied by Lixol (Groupe Berkem, Blanquefort, France). Vinylmethyldimethoxy silane (VMDMS), potassium hydroxide (KOH), t-butyl peroxybenzoate, p-toluenesulfonic acid

(pTSA), chloroform (CHCl₃), xylene were purchased from Sigma Aldrich. All reagents were used as received.

2.2 Synthesis of phosphosilanol oligomer (DOPO-VMDMS)

In a three necked round bottom flask fitted with a condenser, a mechanical stirrer and a nitrogen inlet, 100.00 g (0.463 mol, 1 eq) of DOPO, 61.22 g (0.463 mol, 1 eq) of VMDMS and 0.90 g (4.63 mmol, 1mol %) of tert butyl peroxybenzoate were added. The reaction was carried out to 120 °C during 4 hours. Then, 16.67 g (0.926 mol, 2 eq.) of a water solution of KOH (5 wt%) was added to the reaction mixture and carried out at 80 °C for 2 hours. The mixture has become cloudy due to the insolubility of the oligomer in water. The organic phase was then extracted with 200 mL of chloroform 3 times. The organic phases were combined and dried with magnesium sulfate. Then, they were distilled under reduced pressure to give a white foam, the phosphorus-containing silanol oligomer. The yield was 83 %.

³¹P NMR (202.4 MHz, CDCl₃, ppm): δ: 39.9

¹H NMR (500 MHz, CDCl₃, ppm): δ: -0.42-0.17 (3H, Si-CH₃), 0.47-0.92 (2H, Si-CH₂), 1.69-2.20 (2H, P-CH₂), 7.04-8.09 (8H, aromatics)

²⁹Si NMR (99.3 MHz, CDCl₃, ppm): δ: -21.9

The degree of polymerization was determined by ¹H NMR by using an internal standard and the integration of CH₃-Si. The value found was 3.7 which represents an average degree of polymerization of 4. The phosphorus content was 10.3 wt% and the silicone content was 9.7 wt% in this flame retardant product.

2.3 Synthesis of tall oil fatty acid (TOFA) alkyd resin

A long oil TOFA alkyd resin was prepared by solvent process using TOFA, pentaerythritol, phthalic anhydride and maleic anhydride. 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 was added, followed by phthalic anhydride and maleic anhydride at 200 °C. Reaction mixture was heated to 220 °C using xylene as azeotropic solvent to remove water. The reaction was continued until an acid value of 7 mg of KOH/g of resin was obtained. Xylene was removed by vacuum and then white spirit was added to obtain a solid content of 50 wt%.

TOFA alkyd resins were synthesized to obtain a final hydroxy value around 55 KOH/g, which corresponded to the excess of -OH functions at the end of the synthesis.

2.4 Synthesis of silicone-phosphorus containing TOFA alkyd resin

In order to prepare silicone-phosphorus hybrid alkyd resin, the previously synthesized alkyd resin was reacted separately with 10, 20, 30 and 40 wt% of DOPO-VMDMS content (which respectively represented around 1 wt% of P and Si, 2 wt% of P and Si, 3 wt% of P and Si and 4 wt% of P and Si). TOFA alkyd resin, DOPO-VMDMS and pTSA 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 temperature 160-170 °C under nitrogen atmosphere. In all cases (10, 20, 30 and 40 wt% of DOPO-VMDMS), samples of the reaction mixture were periodically taken out and were monitored by the "clear on plate test". This consists of

applying a drop of samples of resin on a clean glass plate and then observing their clarity after evaporating the solvent. The reaction was carried out until a clear and transparent drop was obtained. It was observed that incorporation of 40 wt% of DOPO-VMDMS into alkyd resins leads to phase separated product. Hence, the modification was carried out up to 30 wt% of DOPO-VMDMS. Moreover, at the end of the reaction a measure of acid value was carried. The results exhibited values identical to the ones measured before the modification with DOPO-VMDMS.

2.5 Characterizations

2.5.1 NMR spectroscopy

NMR samples were prepared with CDCl_3 as solvent and the analyses were performed using a Bruker Avance 500 MHz spectrometer. The structure of DOPO-VMDMS was determined by hydrogen nuclear magnetic resonance (^1H NMR), silicon nuclear magnetic resonance (^{29}Si NMR) and phosphorus nuclear magnetic resonance (^{31}P NMR). External references were trimethylsilane (TMS) for ^1H and ^{29}Si NMR, and phosphoric acid (H_3PO_4) for ^{31}P NMR. Shifts were given in ppm. Diffusion ordered spectroscopy (DOSY) ^1H NMR was used to confirm the grafting of DOPO-VMDMS to the alkyd resin and were performed on a Bruker Avance 600 MHz spectrometer with CDCl_3 as solvent.

The molar mass of one repetition unit was determined by NMR thanks to the equation (1). A known mass of product and 1,3,5-trioxane were poured into a NMR tube and 500 μL of CDCl_3 were added. The NMR titrations were made in triplicate to have an average result. The molar mass of one repetition unit was determined using equation (1) by comparing the integration value of the signals assigned to the 1,3,5-trioxane protons (5.12 ppm) with the integration of the signals arising from Si- CH_3 of the oligomer at -0.13 ppm.

$$Mw_{1 \text{ unit}} = \frac{\int \text{Trioxane} \times H_{\text{Si-CH}_3}}{\int \text{DOPO-VMDMS} \times H_{\text{Trioxane}}} \times \frac{m_{\text{DOPO-VMDMS}}}{m_{\text{Trioxane}}} \times M_{\text{Trioxane}} \quad (1)$$

$Mw_{1 \text{ unit}}$: molar mass of one repetition unit; \int_{Trioxane} : integration of the signal from Trioxane protons; $\int_{\text{DOPO-VMDMS}}$: integration of the signals from protons in Si- CH_3 signal of DOPO-VMDMS oligomer; $H_{\text{Si-CH}_3}$: number of protons in Si- CH_3 of DOPO-VMDMS signal; H_{Trioxane} : number of trioxane protons; $m_{\text{DOPO-VMDMS}}$: product mass; m_{Trioxane} : Trioxane mass; M_{Trioxane} : Trioxane molar mass.

2.5.2 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). Data were analyzed using the software OMNIC Series 8.2 from Thermo Scientific.

2.5.3 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.

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

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

2.5.4 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^{-1} . All the resins were compared at the non-volatile content of 50 wt%.

2.5.5 Size-exclusion chromatography

Molar masses of DOPO-VMDMS 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 $mL \cdot min^{-1}$. 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 $g \cdot mol^{-1}$. The typical sample concentration was 15 $mg \cdot mL^{-1}$.

2.5.6 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⁻¹ between -100 and 100 °C to observe the glass transition temperature.

2.5.7 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 $mL \cdot min^{-1}$ nitrogen flow. The protective gas used was nitrogen with a 20 $mL \cdot min^{-1}$ flow. Approximately 10-12 mg of sample was placed in an alumina crucible and heated from room temperature to 800 °C with a 20 °C·min⁻¹ heating rate.

2.5.8 Pyrolysis combustion flow calorimeter analysis

Fire behavior 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 ($N_2/O_2 = 80/20$). At this temperature and with 20 % of oxygen, combustion was considered to be complete. 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)⁴². All samples were tested in triplicate.

2.5.9 Cone calorimeter test

Flammability was studied using a cone calorimeter to investigate the fire behavior of resins used as coating on wood specimens. The alkyd resins were applied on a 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)⁴³. 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.

2.5.10 Film properties

In order to characterize films properties, the resins were mixed with 5 wt% of mix of driers (cobalt octoate, calcium octoate and zirconium octoate). 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 50 μm in all cases. Adhesion was measured using a cross-cut tester 1 mm BYK according to ISO 2409:2020 standard. The hardness (Persoz hardness) was determined according to ISO 1522:2006 standard with a TQC SP0500 pendulum hardness tester. Gloss was measured based on ISO 2813:2014 standard and the measurements were performed on substrates at 60° and 20° using a TQC Polygloss. The values for the hardness and the gloss measurements were determined at day +6 (D+6) 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 (H₂O), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl)⁴⁴. 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 (3). The analyses were made in triplicate for each sample and the reported residual masses percentage are average values of the three samples.

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

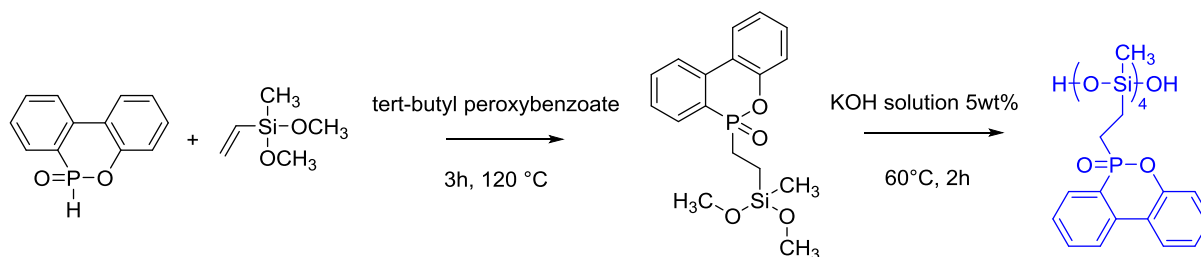
*m*₁: mass of the alkyd resin sample before being immersed in solvent; *m*₂: mass of the alkyd resin sample after being immersed in a solvent and dried in oven.

3. Results and discussion

3.1 Synthesis of TOFA alkyd resin with silicone and phosphorus based flame retardants

The synthesis of DOPO-VMDMS is shown in Scheme 2. This synthesis has been investigated by several teams such as Zhong *et al.*³⁰ and Wang *et al.*⁸ To optimize the yield and the time of the first step of this reaction, DOPO-VMDMS monomer was synthesized in bulk with a radical initiator. DOPO and VMDMS were added in stoichiometric ratio 1:1 and stirred at 120 °C for 4h. This Pudovik reaction allows the labile P-H bond of DOPO to react with

unsaturated double bonds C=C of VMDMS⁴⁵. This reaction follows a radical mechanism thanks to the introduction of 1 mol% of tert-butyl peroxybenzoate, a radical initiator with a half-life time of 75 min at 120 °C.



Scheme 2: Synthesis of phosphosilanol oligomer (DOPO-VMDMS)

DOPO-VMDMS monomer was characterized by ³¹P and ¹H NMR spectroscopy. The NMR spectra are presented in Figure 1a and 1b. The disappearance of signal at 5 ppm in the ¹H NMR spectrum confirms the quantitative reaction of the C=C of VMDMS with the DOPO. Then, in the ³¹P spectrum, the disappearance of the chemical shift at 16 ppm for DOPO and the appearance of the chemical shift at 38 ppm are characteristic of the formation of a new P-C bond.

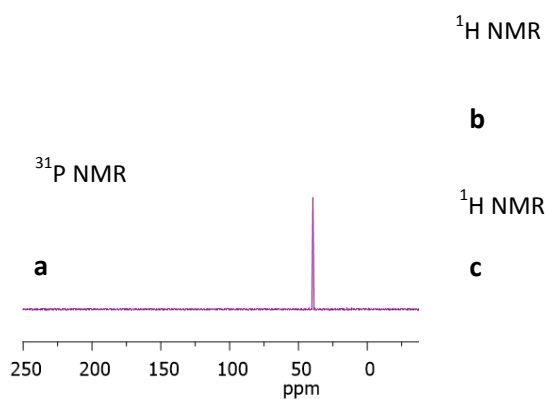


Figure 1: NMR spectra in CDCl₃ of DOPO-VMDMS monomer a) ³¹P NMR, b) ¹H NMR and c) DOPO-VMDMS oligomer ¹H NMR

The second step of the synthesis of the DOPO-VMDMS oligomer was the hydrolysis of Si-OCH₃ into Si-OH and the condensation of Si-OH to form a reactive oligomer thanks to a water solution containing 5 wt% of potassium hydroxide⁴⁶. Hydrolysis occurred through the nucleophilic attack of the oxygen atom of water onto the silicon atom and releases methanol.⁴⁶ Moreover, the use of catalysts such as KOH, provided a faster and a more complete hydrolysis-condensation reaction⁴⁷. The final product of the reaction was analyzed

by ^1H NMR (Figure 1c), which confirmed the absence of signal of $\text{CH}_3\text{-O-Si}$, between 3.25 and 3.60 ppm.

The chemical structure of the oligomer was also confirmed by FTIR analysis (Figure 2). Indeed, the consumption of the P-H group was observed through the disappearance of the absorption peak at 2375 cm^{-1} in Figure 2. Moreover, the appearance of a peak around 3300 cm^{-1} confirmed the DOPO-VMDMS formation by the presence of -OH linked group.

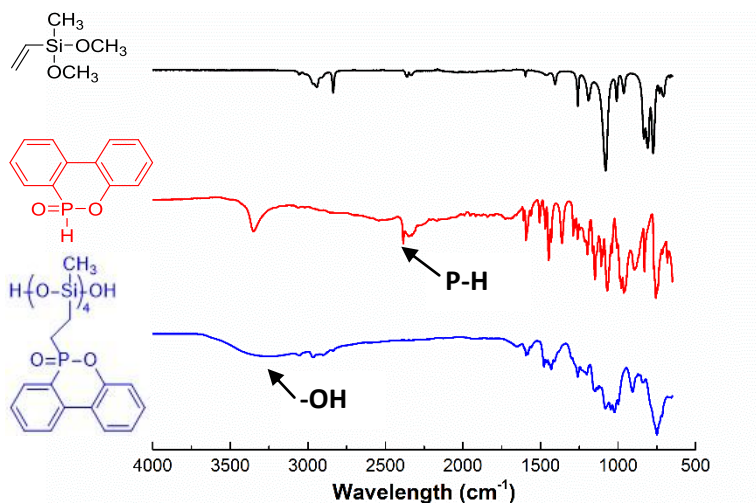
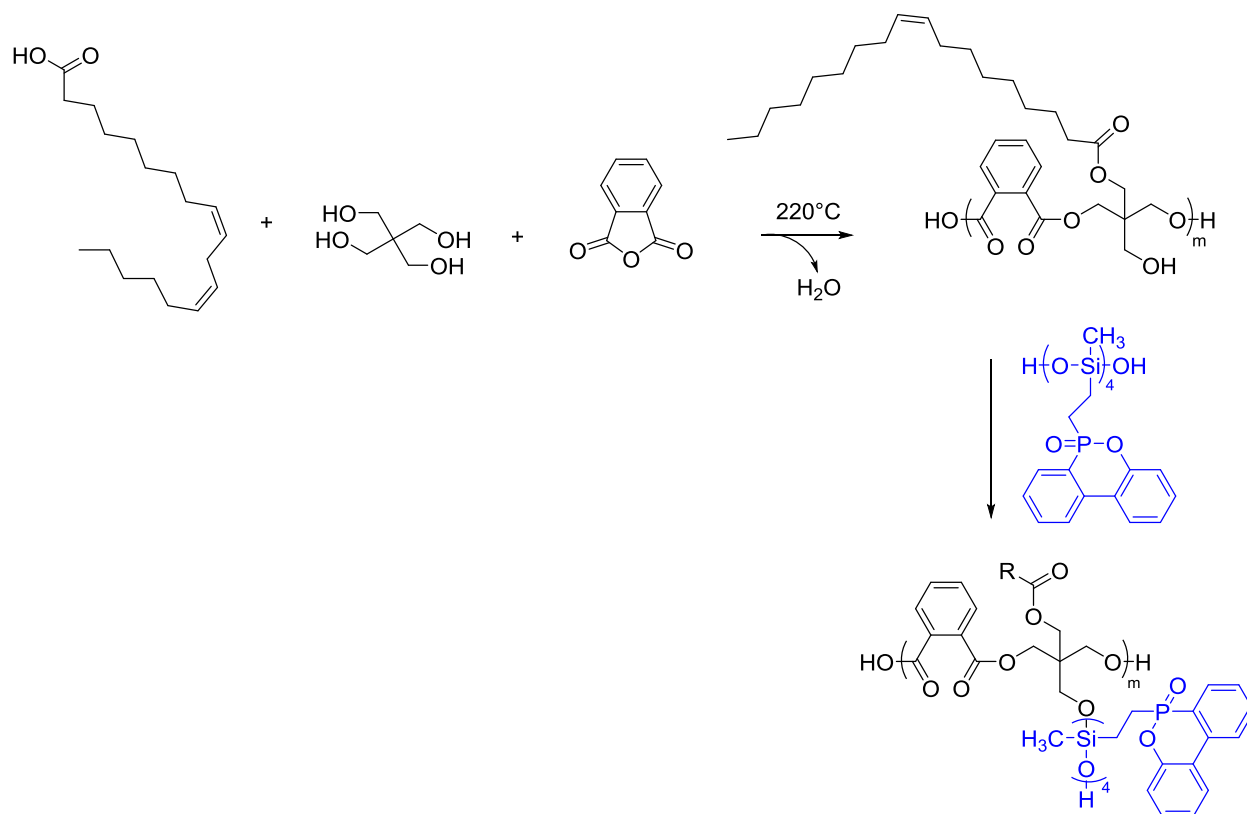


Figure 2: FT-IR spectra of VMDMS, DOPO and DOPO-VMDMS oligomer

The final DOPO-VMDMS is an oligomer. The molar mass of the repetitive unit is $302\text{ g}\cdot\text{mol}^{-1}$. The results from the SEC analyses showed that the number-average molar mass of DOPO-VMDMS oligomer was $1.200\text{ g}\cdot\text{mol}^{-1}$ with a dispersity of 1.3. These results assumed that the average degree of polymerization (n) was equal to 4.

In order to confirm this degree of polymerization, NMR titration using 1,3,5-trioxane as standard in deuterated chloroform was achieved. These results showed a degree of polymerization of 4 in agreement with the SEC analysis.

In this study, alkyd resins have been synthesized through a fatty acid process with the presence of xylene as an azeotropic solvent. The synthesis of tall oil fatty acid (TOFA) alkyd resin is presented in Scheme 3. The resins have been designed to obtain a long oil length⁴⁸ with at least 60 wt% of fatty acids in their composition and the same excess of hydroxyl functions.



Scheme 3: Synthesis of TOFA alkyd resin with silicone and phosphorus based flame retardants

The last step was the condensation of the Si-OH groups of the DOPO-VMDMS oligomer with the unreacted -OH groups of the alkyd resins. The synthesis of TOFA alkyd resin containing silicone and phosphorus- is shown in scheme 3. Table 1 summarizes the amount of alcohol and acid functions introduced for the polycondensation as well as the concentration of DOPO-VMDMS oligomers.

Table 1: Amounts of the reagents for the synthesis of DOPO-VMDMS alkyd resins

Samples	f_{OH} polyol ^b (mol)	f_{COOH} ^b (mol)	f_{OH} DOPO- VMDMS (mol)	f_{OH} excess (mol)	DOPO- VMDMS (wt%)	wt% P	wt% Si
Reference	0.93	0.78	0	0.15	0	0	0
10 wt% ^a	0.91	0.73	0.025	0.155	10	1.03	0.97
20 wt% ^a	0.98	0.80	0.033	0.147	20	2.06	1.94
30 wt% ^a	0.66	0.47	0.038	0.152	30	3.09	2.91
40 wt% ^a	0.60	0.45	0.052	0.15	40	4.12	3.88

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

^b: number of functions at t=0.

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 white particles inside the drop shows an incompatibility between the DOPO-VMDMS oligomer and the alkyd resin. Indeed, the resin is an organic polymer whereas the oligosiloxane is an inorganic substance. When the oligomer is covalently bonded to the alkyd resin, the drop appears transparent as the products are compatible.

However, the bonds between the oligomer and the alkyd resins were also determined by DOSY ¹H NMR (Figure 3). 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 characteristic peak of DOPO-VMDMS oligomer (Si-CH₃) at -0.12 ppm exhibited the same diffusion coefficient as the alkyd resin, at -10 log (m²·s⁻¹). Thus, it confirmed the covalent bond between the two polymers. Side-reactions occurred during the polymerization of the alkyd resins leading to peaks with a diffusion coefficient at -9 log (m²·s⁻¹). DOSY NMR of other alkyd resins are provided in supporting information (SI).

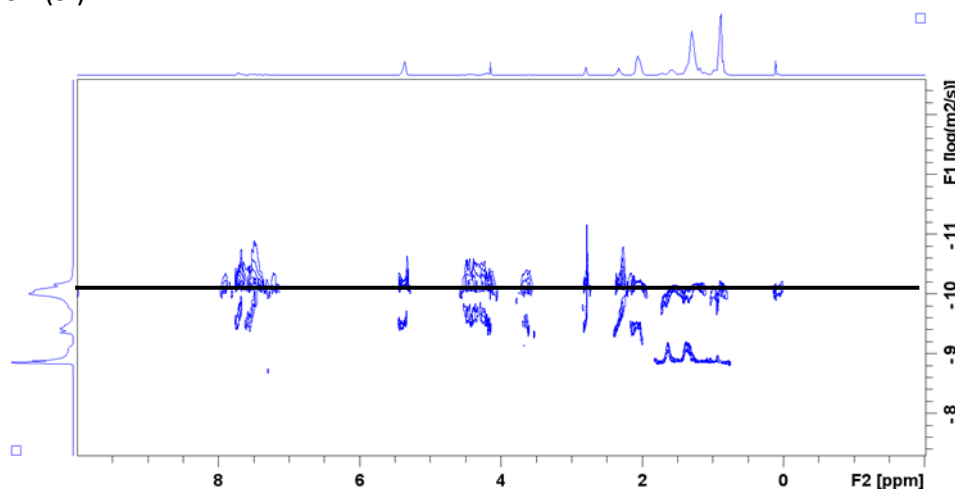


Figure 3: ¹H DOSY NMR of DOPO-VMDMS alkyd resins

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 (PMMA equivalent) are presented in Table 2. As expected, M_n , M_w and \mathcal{D} values increased with the amount of DOPO-VMDMS. Indeed, the oligomer was grafted onto the alkyd resins as a comb structure 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 DOPO-VMDMS oligomer.

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 50wt % and the results are presented in Table 2. Hybrid alkyd resins exhibited a higher viscosity than the reference alkyd resin, which was expected since the molar mass of the FR-free alkyd resin was lower than the DOPO-VMDMS alkyd resins. Moreover, the presence of bulky groups, such as the phenyl groups of

the DOPO, increases the viscosity. Furthermore, the viscosity of hybrid alkyd resins increased from 0.54 Pa·s to 2.72 Pa·s with increasing amounts of DOPO-VMDMS in the resins. Those results are consistent with those obtained by SEC.

Table 2 : SEC values (M_n , M_w and \bar{M}_w) and viscosity of all alkyd resins.

Samples	M_n ($g \cdot mol^{-1}$)	M_w ($g \cdot mol^{-1}$)	\bar{M}_w	η (Pa·s)
Reference	4,500	15,000	3.3	0.11
10 wt% ^a	5,500	20,000	3.5	0.54
20 wt% ^a	6,000	22,000	3.7	1.23
30 wt% ^a	6,500	23,500	3.8	2.72

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

The introduction of a silicone containing compound in the lateral chain of alkyd resin can have a strong influence on the physical properties of the polymer. That is why differential scanning calorimetry (DSC) analyses were performed, to determine the glass transition temperature (T_g), summarized in Table 3. An higher T_g confers more rigidity to the material which was observed with the addition of DOPO-VMDMS oligomer. The alkyd resin without DOPO-VMDMS exhibited a T_g around 10 °C while the resin with 10 wt% DOPO-VMDMS showed a T_g of 19 °C. Furthermore, increasing amounts of DOPO-VMDMS oligomer have a slight influence on the T_g value which varies from 19 °C for the alkyd resin with 10 wt% DOPO-VMDMS to 24 °C for the alkyd resin with 30 wt% DOPO-VMDMS. This evolution was mainly due to the introduction of aromatic groups of DOPO and slightly to the possible crosslinking of silicon chains in alkyd resins.

Table 3: T_g values of the alkyd resins.

Samples	DOPO-VMDMS	Reference	10 wt% ^a	20 wt% ^a	30 wt% ^a
T_g (°C)	43	10	19	19	24

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

3.2 Thermal and flame retardant properties

Analyzes of thermal and flame retardant properties have been studied to highlight the influence of the DOPO-VMDMS oligomer in alkyd resins. The thermal decomposition of the DOPO-VMDMS oligomer occurred in three steps, which can be noticed clearly in the derivative thermogravimetry (DTG) in Figure 4. The maximum weight loss of the first step was observed around 70 °C with a weight loss of 2 %. This weight loss may be caused by the evaporation of residual chloroform used as solvent during the purification of DOPO-VMDMS oligomer. Then, the maximum weight loss of the second step was observed around 175 °C with a weight loss of 4 %. At this temperature, a polycondensation reaction could occur between the silanol groups (Si-OH), releasing water. The maximum weight loss of the third step was observed around 475 °C with a weight loss of 47 %. This degradation may be caused by the decomposition of DOPO that forms PO and PO₂ radicals⁴⁹ but also by the

scission of Si-O-Si groups in DOPO-VMDMS. It is well known that DOPO mainly acts in gaseous phase through the formation of PO radicals with little efficiency as char promoter²³. The thermal properties of all alkyd resins were investigated by thermogravimetric analyses (TGA) under nitrogen flow. Figure 5 shows the thermograms of the alkyd resin, and the modified AR with respectively 10 wt%, 20 wt%, and 30 wt% DOPO-VMDMS oligomer. Thermal stability slightly increased with the DOPO-VMDMS addition. Thermal factors such as the decomposition temperature at 5 % weight loss, temperature at 50 % weight loss, and the residue yield at 750 °C, are summarized in Table 4. Firstly, it was observed that the temperature at 5 % weight loss did not change with the introduction of FR. Those low temperatures could be associated to boiling of residual solvent, such as white spirit or residual xylene, trapped in the polymer matrix during drying.

Considering the temperature at 50 % weight loss ($T_{d,50wt\%}$), the thermal stability was slightly higher for the alkyd resins containing DOPO-VMDMS. Indeed, this temperature varied from 390 °C for the alkyd resins without DOPO-VMDMS to 400 °C for the alkyd resins with 30 wt% DOPO-VMDMS which is of little significance. Moreover, the weight loss rate at $T_{d,max}$ decreased from 76 % for the FR-free alkyd resin to 64 % for the AR with 30 wt% DOPO-VMDMS. The residue yield of FR-free AR was about 14 wt%, while the residue yield of DOPO-VMDMS oligomer was higher, around 40 wt%.

The residue yield of the resin increased with the content of DOPO-VMDMS oligomer, with a maximum at 24 wt% for the alkyd resin containing 30 wt% of DOPO-VMDMS oligomer. The residue yield was promoted by the VMDMS in the oligomer. This residue increase is likely to entail an insulating effect during combustion with cone calorimeter. Indeed, during combustion, SiO₂ acts as a continuous and protective ceramic layer. This carbon-silica layer can insulate the polymer and prevent heat and gas transfer between gas and condensed phases.^{11,21}

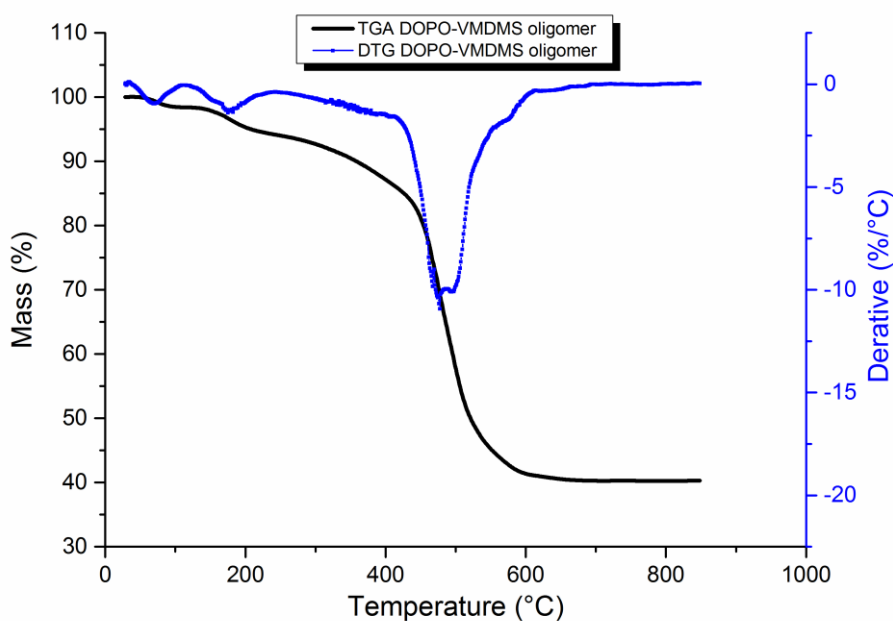


Figure 4: TGA (black) and DTG (blue) curves of DOPO-VMDMS oligomer.

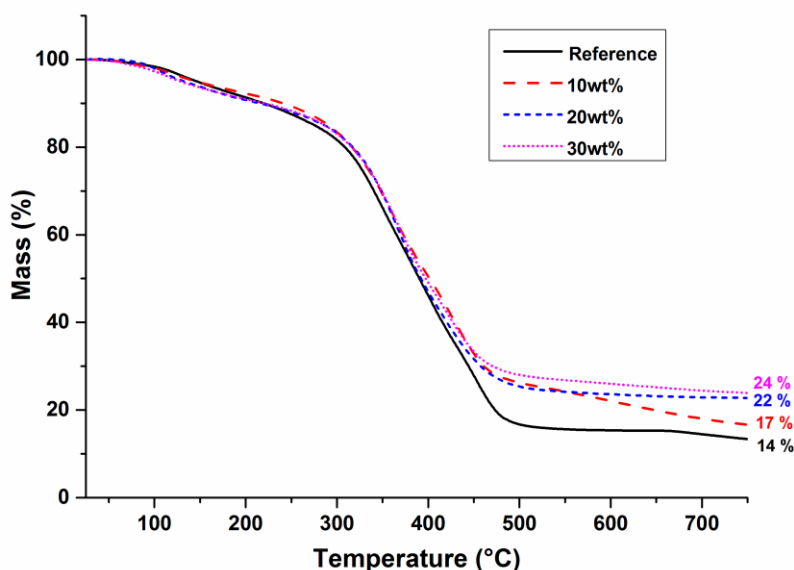


Figure 5: TGA curves of reference alkyd resin and alkyd resins with 10 wt%, 20 wt% and 30 wt% DOPO-VMDMS samples.

Table 4: Results of TGA analyses on alkyd resins and on functional oligomer

Samples	$T_{d,5wt\%}$ (°C)	$T_{d,50wt\%}$ (°C)	$T_{d,max}$ (°C)	Weight loss at $T_{d,max}$ (%)	Residue at 750°C (%)
DOPO-VMDMS	208	521	475	47	40
Reference	137	390	349	76	14
10 wt% ^a	136	399	363	68	17
20 wt% ^a	136	396	365	67	22
30 wt% ^a	135	400	367	64	24

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

Table 5 summarizes the data obtained from PCFC analyses. In standard conditions, combustion is complete in PCFC test due to the combustion chamber at 900 °C under oxygen flow. Therefore, the inhibitory effect of DOPO is not demonstrated in PCFC analysis. The obtained curves are presented in Figure 7 and showed a reduction of pHRR and THR with the increase of the amount of DOPO-VMDMS oligomer in the resin. Indeed, pHRR decreased from 183 W·g⁻¹ for the FR-free alkyd resin to 107-124 W·g⁻¹ for the alkyd resin modified with 30 wt% DOPO-VMDMS. The figure showed that the alkyd resins modified with 20 wt% and 30 wt% of DOPO-VMDMS exhibited two pHRR peaks. An early decomposition of DOPO-VMDMS may explain this phenomenon. This introduction of DOPO-VMDMS in the alkyd resin has showed a small influence on the temperature of the pHRR, which was not significant. Indeed, the higher T_{pHRR} were 427 °C for the FR-free alkyd resin, and respectively

416 °C, 438 °C, 435 °C for the alkyd modified with 10 wt%, 20 wt% and 30 wt% DOPO-VMDMS. THR slightly decreased with increasing amounts of DOPO-VMDMS, from 19.4 $\text{KJ}\cdot\text{g}^{-1}$ for the FR-free alkyd resin to 17.3 $\text{KJ}\cdot\text{g}^{-1}$ for the 30 wt% DOPO-VMDMS alkyd resin. The residual content after anaerobic pyrolysis increased from 7 wt% to 23 wt% for the FR-free resin and the resin with 30 wt% DOPO-VMDMS respectively. This 16 % increase was consistent with the TGA results and demonstrated the formation of a char layer and furthermore confirmed the action in condensed phase of the DOPO-VMDMS oligomer. Moreover, the energy of combustion (EHC) slightly increased with the amount of DOPO-VMDMS.

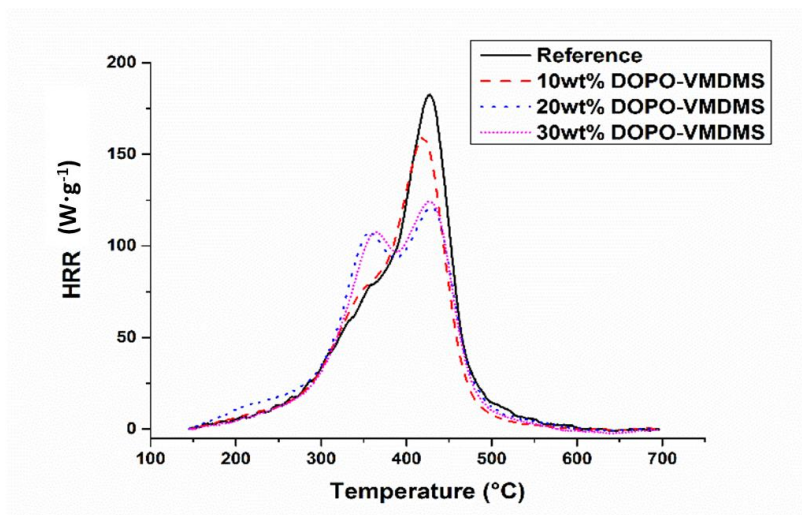


Figure 4: PCFC curves of reference alkyd resin and alkyd resins with 10 wt%, 20 wt% and 30 wt% DOPO-VMDMS samples.

Table 5: Results of PCFC tests on alkyd resins

Samples	$p\text{HRR}$ ($\text{W}\cdot\text{g}^{-1}$) ¹⁾	T at $p\text{HRR}$ ($^{\circ}\text{C}$)	THR ($\text{KJ}\cdot\text{g}^{-1}$)	Residue content (%)	EHC ($\text{KJ}\cdot\text{g}^{-1}$) ¹⁾
Reference	183	427	19.4	7	20.9
10 wt% ^a	159	416	18.6	13	21.4
20 wt% ^a	107 and 124	358 and 438	17.8	19	21.9
30 wt% ^a	108 and 121	365 and 435	17.3	23	22.5

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

The cone calorimeter analyses provide important information on the fire behavior of a material⁵⁰. Cone calorimeter tests were performed with a heat flux of $35 \text{ kW}\cdot\text{m}^{-2}$ under ventilated conditions. The results are summarized in Table 6. Figure 8 shows the cone calorimeter curves. Tests were performed on wood samples with around 1 g of dry resin as coating. The rate of heat release (HRR) as well as the total heat release (THR) are important parameters to characterize the fire performance of materials. All the curves present two $p\text{HRR}$ which is very common for wood samples. The first peak represents the heat release rate ($p\text{HRR}_1$) reached just after the ignition. After the completed consumption of the coating,

the heat flux decreases until reaching a plateau which corresponds to the heat penetrating the wood until reaching the bottom of the sample. The lower is the plateau, the slower the pyrolysis progresses through the thickness of the wood. When the heat reaches the unexposed surface (insulated by rockwool), it cannot be evacuated, leading to a second peak of heat release rate (pHRR₂). This second peak of heat release rate is induced by the wood and its thickness and is independent on the coating. All the samples have a wood thickness around 25 mm ± 0.2 mm. Wood without coating presents a moderate pHRR₁ at 190 KW·m⁻². The use of a coating layer generally negatively affects the flame retardancy of wood, but offers protection against external aggressions such as UV, weather, insects. The objective was to provide a coating with better flame retardancy than a standard coating. Indeed, the FR-free alkyd resin leads to a strong enhancement of the pHRR₁ (up to 337 kW·m⁻²). The introduction of DOPO-VMDMS in the alkyd resin had a strong influence on the pHRR due to its activity in both condensed and gas phases. Indeed, pHRR₁ decreased with increase amounts of DOPO-VMDMS. The lowest pHRR₁ was obtained with 30 wt% DOPO-VMDMS in the matrix polymer. The introduction of up to 30 wt% DOPO-VMDMS into the alkyd resins has improved flame retardancy by decreasing the pHRR₁ from 337 KW·m⁻² to 160 KW·m⁻² which corresponds to a decrease by almost 55 % compared to the FR-free alkyd resin. The energy of combustion (EHC) of alkyd resins slightly decreased with increasing amounts of DOPO-VMDMS from 12.5 MJ·Kg⁻¹ for the FR-free alkyd resin to 11.2 MJ·Kg⁻¹ for the alkyd resin with 30 wt% DOPO-VMDMS. Nevertheless, the presence of a coating did not have a significant influence on the combustion energy. Indeed, this energy was calculated from the residual mass and the THR which corresponded to the release of heat throughout the analysis and not only for the pHRR₁ whereas the coating only had an effect on the pHRR₁. Moreover, the coating was the only difference between all the samples and had negligible mass. Time to ignition (TTI) measures the time to achieve sustained flaming combustion at a particular cone irradiance. TTI strongly decreased with the introduction of DOPO-VMDMS from 47 s for the FR-free alkyd resin to 11 s for the resin with 10 wt% DOPO-VMDMS. All the alkyd resins with DOPO-VMDMS exhibited a TTI around 10 s. While DOPO mainly acts as a flame inhibitor, an increase of the TTI was expected. However, the unexpected reduction of TTI may be caused by the early decomposition of DOPO-VMDMS. Indeed, the decomposition of DOPO-VMDMS oligomer occurs in three steps as showed on the derivative DTG curve in Figure 7.

Smoke production rate (SPR) represented in Figure 9 provided additional information about the mode-of-action of DOPO-VMDMS in cone calorimeter test. Indeed, a significant increase in smoke production is usually due to flame inhibition. As expected, coatings containing alkyd resins with DOPO-VMDMS exhibited higher SPR than the wood and the alkyd resin without DOPO-VMDMS. These observations showed that DOPO-VMDMS acted in gas phase thanks to the release of flame inhibitor.

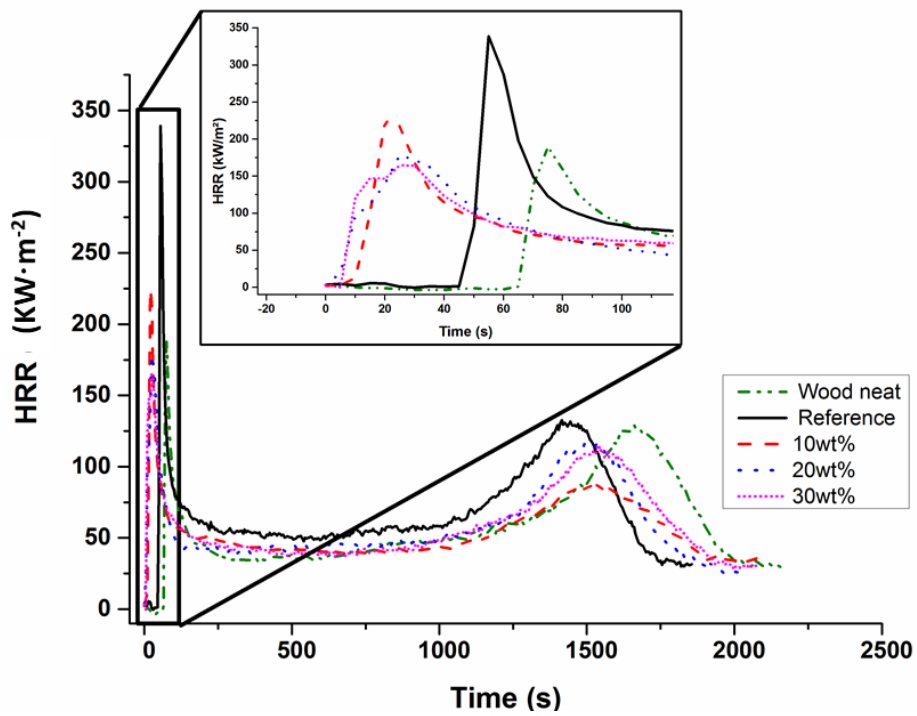


Figure 5: Curves of cone calorimeter tests for wood, reference alkyd resin and alkyd resins with 10 wt%, 20 wt% and 30 wt% DOPO-VMDMS samples.

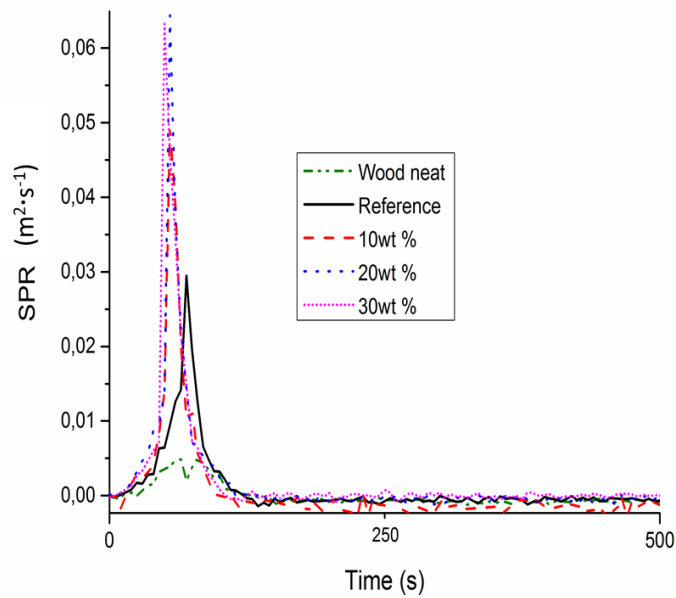


Figure 6: Smoke production rate curves for wood, reference alkyd resin and alkyd resins with 10 wt%, 20 wt% and 30 wt% DOPO-VMDMS samples.

Table 6: Results of cone calorimeter tests at heat flux 35kW·m²

Samples	TTI (s)	pHRR ₁ (KW·m ⁻²)	THR (MJ·g ⁻¹)	EHC (MJ·Kg ⁻¹)
Wood neat	65	190 ± 10	9.4	11.8
Reference	47	337 ± 9	10.2	12.5
10 wt% ^a	11	245 ± 16	10.1	12.2
20 wt% ^a	6	183 ± 12	9.1	11.5
30 wt% ^a	8	160 ± 9	9.3	11.2

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

3.3 Film properties

Films of the different resins have been applied with a film applicator to obtain dry films with a thickness of 50 µm. Adhesion, flexibility, gloss, drying time and chemical resistance have been determined and the results are presented in the following section in Table 7 and Table 8.

Table 7: Adhesion, flexibility, gloss and drying time value of the alkyd resins.

Samples	Adhesion	Hardness (s)	Gloss 20°/60°	Drying time (min)
Reference	0	92	60/92	270
10 wt% ^a	0	81 ^b	66/94	200
20 wt% ^a	0	95	80/97	190
30 wt% ^a	0	119	81/96	180

^a: represent the mass percentage of DOPO-VMDMS introduce in the alkyd resin.

^b: for the analysis, the film was “sliding”, conducting the pendulum to shift from its initial position under the effect of the pulsed kinetic energy. The value may actually be higher than that specified.

3.3.1 Adhesion

The adhesion tests were performed according to the ISO 2409:2020 standard (characteristics of the standard are provided in SI). 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 which corresponds to a class 0. The introduction of DOPO-VMDMS in alkyd resins did not impact the adhesion properties of the resins.

3.3.2 Hardness

The hardness of the coating was determined according to the ISO 1522:2006 standard (method explained in SI). One second corresponds to one oscillation of the pendulum. 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 92 for the reference resin to 119 for the resin with 30 wt% of DOPO-VMDMS. It means that the introduction of DOPO-VMDMS in alkyd resins provides harder films. Moreover, the hardness increased with the quantity of DOPO-VMDMS. These results are in agreement with the DSC results which showed higher T_g values with the increase of DOPO-VMDMS amount in alkyd resins. Nevertheless, even with increased values of hardness for the resins modified with DOPO-VMDMS, the values were closed to the reference resin. It means that the films remained flexible allowing the resin to maintain its films-forming properties for wood and metal substrates.

3.3.3 Gloss

The values of gloss of the coatings were determined according to ISO 2813:2014 (method is explained in SI). Firstly, the measurement was made at 60 ° to determine the gloss level. All the alkyd resins exhibited a high gloss level with values between 92 and 96. The measurement was then made at 20 °. The reference resin showed a value of 60 whereas the resin with 30 wt% DOPO-VMDMS exhibited a value of 81. The introduction of DOPO-VMDMS increased the gloss value of the coating. Moreover, the gloss value of the silicone-alkyd hybrid resins increased slightly with the content of silicone introduced. Those results were expected because it had been reported that silicone-alkyd hybrid resins have excellent gloss properties.⁴⁰

3.3.4 Drying time

The introduction of DOPO-VMDMS oligomer in the alkyd resins highly reduced the drying time of the resins. Nevertheless, the concentration of DOPO-VMDMS in the resin had only a slight impact on the reduction of drying time. This reduction was related to a higher molar mass and is also favored by the increase of the T_g of the alkyd resins with DOPO-VMDMS. Indeed, the higher rigidity brought by the DOPO-VMDMS led to the formation of a “solid” film at an earlier step of crosslinking⁴⁸.

3.3.5 Chemical resistance

Table 8 presents the results of the determination of 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. The chemical resistance of the alkyd resins in water was slightly better for silicone-alkyd hybrid resins. Indeed, all the silicone-alkyd hybrid resins exhibited a residual mass percentage of 80 % compared to the 76 % of the FR-free alkyd resin. Nevertheless, this difference was not significant. The chemical resistance in HCl presented a residual mass percentage just above 50 %. Alkyd resins were highly resistant to NaCl solution with a residual mass superior to 95 %. There was a slight increase in NaCl resistance for the alkyd resins with DOPO-VMDMS. In the case of NaOH solution, the alkyd resins resistance was very low with the best result obtained for the alkyd resins with 20 wt% and 30 wt% DOPO-VMDMS. Indeed, those resins increased by 6 % the residual mass compared to the FR-free alkyd resin. The poor resistance to alkali can be due to hydrolysable ester groups in the alkyd resins^{44,51}. The introduction of DOPO-VMDMS did not seem to have a strong influence

on the chemical resistance. Indeed, it has been demonstrated that chemical resistance is related to the crosslinking degree of the alkyd resins³³.

Table 8: Chemical resistance of the alkyd resins.

Samples	Water	HCl (0.1 M)	NaOH (0.1 M)	NaCl (5 %)
Reference	76 % ± 2 %	54 % ± 3 %	12 % ± 4 %	96 % ± 1 %
10 wt% ^a	80 % ± 1 %	56 % ± 4 %	17 % ± 3 %	99 % ± 0.5 %
20 wt% ^a	80 % ± 0.5 %	55 % ± 2 %	19 % ± 2 %	99% ± 0.5 %
30 wt% ^a	80 % ± 1 %	56 % ± 2 %	19 % ± 1 %	99 % ± 0.5 %

^a: represent the mass percentage of DOPO-VMDMS introduced in the alkyd resin.

4. Conclusion

A new flame-retardant oligomer containing phosphorus and silicone (DOPO-VMDMS) has been successfully synthesized. Moreover, the DOPO-VMDMS oligomer has been characterized and grafted onto alkyd resins with suitable characteristics in order to obtain a hybrid polymer with flame retardant properties. The introduction of DOPO-VMDMS oligomer did not deteriorate the chemical resistance of the alkyd resins and drying time, hardness and gloss of the coating have been improved. The synthesis of silicone-alkyd hybrid does not overcome the limits of alkali resistance. However, the viscosity has been modified and increased by the addition of DOPO-VMDMS, as expected. The fire behavior of those polymers has been investigated by TGA, PCFC and cone calorimeter. All the alkyd resins exhibited better thermal behavior with DOPO-VMDMS. It has been demonstrated that the alkyd resin with 30 wt% DOPO-VMDMS provided better thermal resistance and flame retardancy. The residue was also favored with the amount of DOPO-VMDMS. Indeed, TGA and PCFC analysis demonstrated the action of DOPO-VMDMS in condensed phase whereas cone calorimeter analysis exhibited an action in gas phase. DOPO-VMDMS oligomer acted in both phases, demonstrating a synergistic effect between phosphorus and silicon. Wood protected with a coating containing 30 wt% DOPO-VMDMS exhibited a 55 % reduction in pHRR compared to the FR-free coating.

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