



# Article Preparation and Characterisation of UV-Curable Flame Retardant Wood Coating Containing a Phosphorus Acrylate Monomer

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Abstract: The application of a flame retardant coating is an effective solution to enhance the fire retardancy of wood flooring. However, finding the right balance between reducing the flame propagation and good overall coating properties while conserving wood appearance is complex. In order to answer this complex problem, transparent ultraviolet (UV)-curable flame retardant wood coatings were prepared from an acrylate oligomer, an acrylate monomer, and the addition of the tri(acryloyloxyethyl) phosphate (TAEP), a phosphorus-based monomer, at different concentrations in the formulation. The coatings' photopolymerisation, optical transparency, hardness, water sorption and thermal stability were assessed. The fire behaviour and the adhesion of the coatings applied on the yellow birch panels were evaluated, respectively, using the cone calorimeter and pull-off tests. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses were performed on the collected burnt residues to obtain a better understanding of the flame retardancy mechanism. Our study reveals that phosphorus monomer addition improved the coating adhesion and the fire performance of the coated wood without impacting the photopolymerisation. The conversion percentage remained close to 70% with the TAEP addition. The pull-off strength reached 1.12 MPa for the coating with the highest P-monomer content, a value significantly different from the non-flame retarded coating. For the same coating formulation, the peak of heat release rate decreased by 13% and the mass percentage of the residues increased by 37% compared to the reference. However, the flame-retarded coatings displayed a higher hygroscopy. The action in the condensed phase of the phosphorus flame retardant is highlighted in this study.

Keywords: flame retardant; wood coating; phosphorus acrylate; UV-curable coating

# 1. Introduction

With sustainability questions arising in recent decades, wood is more than ever a material of choice for construction. When this renewable resource is supplied from sustainable forests, wood transformation and use are key in the reduction of the energy embodied in building materials. Along with the use of biobased materials, wood constructions provide further energy and greenhouse gas emission savings. In a perspective of limiting global warming, industries are encouraged to replace high-carbon materials with lower-carbon alternatives and when possible, with products based on renewable materials [1]. Hence, using wood instead of steel or cement in the construction sector is one example of emission reduction options. Used since a long time ago for its mechanical properties and visual aspect, wood can be used for both structural and appearance products such as floors, wall panels, ceiling tiles and mouldings [2]. However, the construction industry has to face one limitation of wood: its flammability. To promote their use in non-residential buildings,



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). increasing flame retardancy is thus essential. Different strategies can be employed to improve the fire performance of wood, including the impregnation of flame retardants and the application of flame retardant coatings [3]. In the flooring industry, the second option is usually preferred as it is easier to implement.

Achieving flame retardancy by the application of a flame retardant (FR) coating is mainly dependent on its formulation and the incorporation of FR components. There are different types of flame retardants, the main ones being halogenated compounds, mineral fillers as well as phosphorus- and nitrogen-based compounds. The phosphorus FR have gained interest in recent decades [4]. Phosphorus-based FR may combine a flame retardancy action in the gaseous phase and in the solid phase [5]. Upon phosphorus FR decomposition, various radicals are released including PO $\bullet$  or HPO<sub>2</sub> $\bullet$  [6]. These are able to react by radical recombination with the highly reactive hydrogen H• and hydroxy OH• radicals present in the flame. Consequently, oxidation reactions in the flame are slowed down. The production of heat being reduced, flame propagation is limited. The action of the phosphorus FR in the solid phase mainly results in its contribution to the char formation by esterification and dehydration [6-8]. The generation of acid species upon temperature elevation leads to further reactions with the surrounding polymer matrix and its decomposition by-products. The efficacy of the phosphorus FR is strongly related to its decomposition products' interaction with the chemical environment in the pyrolysis zone [9].

High-solid-content ultraviolet (UV)-curable coating is the most common technology used in the manufacturing of pre-finished flooring. The finishing system is typically composed of a stain, a tie coat, sealer layers and a topcoat. These coatings are most of the time acrylate based, as this technology offers an overall good price/property balance. The curing is performed within seconds and no drying step is required, offering a time gain compared to waterborne or solvent-borne coatings. The obtained coatings achieve good hardness and excellent chemical resistance [10–12].

In this context, the development of P-containing UV-curable coatings to improve the fire performance of wood may represent an interesting approach to widen the use of wood in the construction industry. Few studies deal with transparent UV-curable coatings offering a good flame retardancy of coated wood while still preserving its appearance [13–18]. The addition of FR monomers, reactive diluents, is generally the investigated approach. Chambhare, Lokhande et al. studied phosphorus- and nitrogen-based monomer addition in UV-curable wood coating formulations by adding, respectively, the tris-diethanolamine spirocyclic pentaerythritol bisphosphorate and a difunctional (hydroxypropyl methacrylate) piperazine modified with cyclic phosphates [19,20]. They reported an improved fire and water resistance, higher crosslinking density, but a loss of adhesion on wood. However, the flame retardancy has only been assessed on the coating and not on the coating/wood assembly. Naik et al. also reported the preparation of FR wood coating based on phosphorus and silicon monomers [21]. The coating showing a good adhesion and hardness as well as the best UL-94 rating was a blend with both monomers. The authors attributed the enhancement in flame retardancy to the synergistic effect of phosphorous and silicon. A similar study was conducted with a P,N-containing monomer [22]. In both studies, the intrinsic flame retardant properties of the coatings were assessed by the UL-94 test and the limiting oxygen index (LOI) assessment. The synergy of three monomers containing, respectively, P, S and N elements, the triallyl orthophosphate, the pentaerythritol tetrakis (3-mercaptopropionate), and, the N-dimethylacrylamide, was also investigated in another publication [14]. UV-curable coating formulations were applied on Chinese fir wood samples and UL-94 tests were performed. After fire exposure, the authors reported the formation of an intumescent char layer for some coatings thanks to the release of NH<sub>3</sub> and  $CO_2$ , non-flammable gases during the degradation process. In those studies, the mechanical properties of the coatings were not always thoroughly studied. Furthermore, it appears that the flame retardancy characteristic of the coatings is not systematically assessed in the final condition of use, particularly on the wood/coating assembly.

By enlarging the literature review of acrylic-based FR coatings to non-wood applications, a monomer seems particularly interesting, namely the tri(acryloyloxyethyl) phosphate (TAEP). The fire retardancy of the monomer has already been highlighted in several studies [23–25]. The synthesis of the trifunctional phosphate acrylate monomer was firstly reported by Liang and Shi [26]. They further studied the thermal degradation of different blends of the TAEP monomer with an epoxy acrylate oligomer or with a polyurethane one [23]. The LOI improved with an increased TAEP content. The highest loading allowed to reach a V0 rating at the UL-94 test for both oligomer mixes. With the thermal degradation of the TAEP phosphate groups, polyphosphoric acids were formed, contributing to the char development. The authors highlighted a particularly effective degradation catalysation action on the epoxy acrylate oligomer. The TAEP addition to an epoxy acrylate oligomer led to a viscosity decrease while promoting the photopolymerisation rates and the thermal stability of the UV-cured resins [24]. The authors reported a V0 rating during the UL-94 test with a TAEP content of 50% in the formulation. TAEP was also used to prepare a siliconcontaining hyperbranched polyphosphonate acrylate (HPA), which was then blended with an epoxy acrylate oligomer [25]. In this study, Wang et al. also highlighted the effectiveness of the phosphorus derivative to catalyse the degradation of the oligomer, helping in the formation of a char layer. The transparent HPA-based coatings displayed an improved LOI value and a decreased pHRR and THR. However, the coatings failed to reach a V0 rating for the UL-94 classification with the FR addition. TAEP was also used to develop a FR coating for polyester fabrics [27]. The textiles were plasma-treated before being dipped in the FR formulations and then exposed to UV light. The authors reported an excellent flame retardant property obtained from dipping the fabrics in a blend of TAEP with another FR compound, a 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) derivative. The improved washing resistance was attributed to the surface plasma treatment.

Using flame-retarded UV-curable finishing layers could be a strategy to achieve the flame retardant performances of flooring. However, there is no solution thoroughly described in the literature that enables to fulfil all the specifications targeted. The aim of this present work is thus to evaluate the use of TAEP in a high-solid-content UV-curable wood sealer coat formulations not only with regard to the fire properties but also the other key performances expected from a coating. High-solid-content UV-curable coatings were thus prepared with different phosphorus monomer percentages. Two layers were applied on wood samples, with a low thickness of 25  $\mu$ m per coat. The photopolymerisation kinetics were monitored by photo-differential scanning calorimetry (photo-DSC). The coating optical transparency was measured as a wood flooring coating is usually expected to preserve or improve wood appearance. Other coating properties such as hardness, water sorption and thermal stability were also studied. The wood coating adhesion was evaluated by pulloff tests. This study also highlights the flame retardance behaviour of the wood/coating assembly, studied by cone calorimetry. Scanning electron microscopy (SEM) and energydispersive spectroscopy (EDS) analyses were performed on the collected residues after the cone calorimetry test to complete the characterisation of the FR coating property.

## 2. Experimental Section

# 2.1. Materials

The coatings were prepared with different phosphorus monomer concentrations. Formulations are presented in Table 1. They are based on typical formulations used as sealers for prefinished wood flooring. Both the difunctional epoxy acrylate oligomer (referred as oligomer) and the acrylate monomer tripropylene glycol diacrylate (TPGDA) were supplied by Arkema (Burlington, ON, Canada). The photoinitiator, 2-hydroxy-2-methylpropiophenone (Sigma-Aldrich, Oakville, ON, Canada), was added at 3 wt%. A polybutadiene additive (Cray Valley, Stratford, CT, USA) was used for its defoaming properties at 0.01 wt% in the formulation. All products were graciously provided by Canlak (Daveluyville, QC, Canada).

Raw Material	F0	F1	F2
Oligomer	47.0	47.0	47.0
TPGDA	50.0	30.9	11.7
TAEP	0.0	19.1	38.3
Ricon 130	0.01	0.01	0.01
Photoinitiator	3.0	3.0	3.0

Table 1. Composition of the UV-curable wood coating formulations.

The phosphorus monomer, TAEP, was prepared by the addition of phosphorus oxychloride to hydroxylethyl acrylate (Sigma-Aldrich, Oakville, ON, Canada) following the synthesis described by Liang and Shi [26]. All the products were used as received without further purification. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and Fourier-transform infrared spectroscopy (FTIR) analyses, respectively, displayed in Figures S1 and S2 in the supplementary information, showed the expected structure of TAEP. Its phosphorus concentration was also confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis.

Yellow birch (*Betula alleghaniensis* Britt.) 4.5 mm thick lamellas were provided by Mirage (Saint-Georges, Canada). Raw sawn planks were placed in a conditioning room until mass equilibrium. Relative humidity was set at 42% and temperature at 23 °C, allowing wood samples to reach a moisture content of approximately 8%. Wood samples free from knots and defects were used in this study.

## 2.2. Sample Preparation

Depending on the analysis performed, coatings were either applied on wood samples, steel plates (Type R Q-panels, Q-LAB, Westlake, OH, USA) or on glass panels cleaned with ethanol.

Sample preparation occurred in different stages as shown on Figure 1, with the example of the steps followed prior to the cone calorimeter test. Before coating applications, the wood sample surface was prepared using a 3-step gradual sanding. A first pass was performed at a P-120-grit, then P-150 and the sanding was finalised at P-180. To do so, an automatic sander 36 CCK 1150 (Costa levigatrici S.p.A., Schio, Italy) equipped with paper sanding belts (aluminium oxide type, Abrasifs JJS Inc., Newmarket, ON, Canada) was used.

Prepared formulations were homogenised using a spatula and placed in an ultrasonic bath during 15 min for degassing before use. Formulation viscosity was measured with a piston-type viscometer (ViscoLab 4100, Cambridge Applied Systems Inc., Boston, MA, USA) at 23 °C. Coatings were applied on wood samples, glass or steel plates with a 25  $\mu$ m wire-wound rod (BYK Gardner, Columbia, SC, USA). To be closer to what is performed in the industry, it was applied in two layers, each of 25  $\mu$ m. Before applying the second layer, the coating surface was lightly sanded with a P-400-grit paper to promote interlayer adhesion. A 4-sided applicator (BYK Gardner, Columbia, SC, USA) was used for the application when a higher film thickness was necessary for characterisation tests. When the free films were required, coatings were applied on glass panels, cured, and then carefully pealed of the substrate with a razor blade.

Curing was performed under a medium-pressure mercury vapour lamp on a conveyor at a 5 m·min<sup>-1</sup> speed under atmospheric conditions. Lamp intensity was set at 500 mW·cm<sup>-2</sup>, corresponding to an energy dose of 430–450 mJ·cm<sup>-2</sup> in the UVA range. The intensity and energy doses were measured before and after curing with a Power Puck II radiometer (EIT, Leesburg, VA, USA).



Figure 1. Wood sample preparation for the cone calorimeter test.

#### 2.3. Study of the Coating Photopolymerisation

The impact of trifunctional phosphorus monomer addition on the curing behaviour was monitored by photo-DSC. A DSC822e differential scanning calorimeter (Mettler Toledo, Columbia, USA) coupled with a Lightningcure LC5 mercury-xenon lamp (Hamamatsu Photonics K.K., Iwata, Japan) was used in order to measure the enthalpies of reaction during photopolymerisation. To ensure repeatability, lamp intensity was verified with a radiometer (C6080-02, Hamamatsu Photonics K.K., Iwata, Japan). Experiments were performed under air atmosphere at 30 °C. A coating drop of 2.5  $\pm$  0.1 mg was centred in an open aluminium pan. The sample was then irradiated for 60 s at 50 mW  $\cdot$  cm<sup>-2</sup>. Each formulation was tested four times. All DSC exotherms were normalised to sample weight. The photopolymerisation exotherms resulting from photo-DSC allow the calculation of Rp, the rate of polymerisation, the unsaturation conversion and  $t_{ind}$ , the induction time. The induction time corresponds to the necessary time to achieve 1% of conversion. The polymerisation rate Rp and the conversion percentage were calculated according to Equations (1) and (2), respectively. Both depend on  $\Delta H_{theol}$  the theoretical heat flow for the complete conversion of the acrylate system expressed in  $J \cdot g^{-1}$ . For calculations, a value of 86 kJ·mol<sup>-1</sup> was taken for the heat of the polymerisation per acrylic unsaturation [28]. dH/dt corresponds to the measured heat flow at time t and  $\Delta H_t$  to the heat flow generated up to time *t*.

$$Rp = \frac{(dH/dt)}{\Delta H_{theo}} \tag{1}$$

$$\%_{Conversion} = \left(\frac{\Delta H_t}{\Delta H_{theo}}\right) \times 100$$
 (2)

#### 2.4. Characterisation of the Coating

The coating optical transparency was evaluated by transmittance on a Cary 60 ultravioletvisible (UV–Vis) spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). Analyses were carried out on 100  $\mu$ m thick free films with a scanning wavelength ranging from 400 to 800 nm and using a medium scanning speed (600 nm·min<sup>-1</sup>). An approximation of the glass transition temperature (T<sub>g</sub>) and the crosslinking density of the cured films were calculated from dynamic mechanical analysis (DMA) measurements, performed on a DMA Q800 supplied by TA Instruments (New Castle, USA). DMA apparatus was operated in a tensile mode with the frequency set at 1 Hz and the amplitude at 10  $\mu$ m. A force track of 125% was applied. Measurements were performed at a constant heating rate of 3 °C·min<sup>-1</sup> in a temperature range from 30 °C to 150 °C. Coating-free films were laser cut in a rectangular shape of 25 mm per 5 mm, with a thickness of approximately 100  $\mu$ m. Prior to the test, films were dried at 100 °C during 24 h to avoid any influence of entrapped water. Five repetitions were run per coating formulation. The storage modulus (*E'*) and loss modulus (*E''*) resulting from the dynamic mechanical analysis allow the calculation of the loss factor (tan  $\delta$ ), defined as the ratio of *E''* over *E'*. The storage modulus (*E'*) represents the elastic portion, while the loss modulus (*E''*) characterises the viscous behaviour of the material. In this study, the maximum of the loss factor was used to approximate the glass transition temperature. The crosslinking density was calculated according to Equation (3). *E'* min corresponds to the minimum of storage modulus expressed in Pa, *T* is the temperature at the minimum of storage modulus and *R* refers to the ideal gas constant.

$$\nu_{LD} = \frac{E'_{min}}{3RT} \tag{3}$$

Pendulum hardness tests were performed according to the standardised test method ASTM D4366-16 using a König pendulum tester (BYK Gardner, Columbia, USA). The pendulum was placed on the coating applied on a glass plate and set at a 6° angle to the coating surface normal. The number of oscillations were recorded during pendulum damping from a 6° to 3° angle. Five replicas per formulations were tested for the calculations of the mean values and standard deviations. Dynamic instrumented indentations were carried out on a Micro-Combi tester (CSM Instruments, Peseux, Switzerland) with a diamond Berkovich indenter calibrated on fumed silica beforehand. The indenter tip was led normal to a coating surface applying a maximum load of 300 mN. The force was gradually applied in 5 s, held during 2 s before being unloaded on a 3 s period. Indentation tests were performed 5 times for each sample, on at least 3 repetitions per formulation. For this test, coatings were applied on steel panels with a thickness of 125  $\mu$ m. Higher thickness than the attended application is mandatory in order to have an adequate indenter penetration depth. Steel panels were preferred over wood to ensure substrate hardness homogeneity. Water content was determined with an 890 Titrando titrator for volumetric Karl Fischer titrations equipped with the software Tiamo<sup>TM</sup> Light (Metrohm AG, Herisau, Switzerland). Coating flakes with a thickness of 100  $\mu$ m were dispersed in N,N-dimethylformamide and then placed in an ultrasonic bath for an hour prior to the Karl Fischer titrations. The analyses were performed twice per formulation. To assess the potential influence of adding phosphorus derivatives on the water uptake of the coating films, sorption and desorption isotherms were performed in triplicate on 10 mg film samples with a thickness of 100  $\mu$ m. Before the experiments, the samples were dried overnight in an oven at 100  $^{\circ}$ C. Tests were performed on a DVS Adventure water vapour sorption analyser (Surface Measurement Systems, Allentown, USA) at a constant temperature of 25 °C. First, a step at 0% relative humidity (RH) was performed to allow mass stabilisation. Then, RH was increased from 0% to 95% by means of 5% steps and scaled back down using the same increment. The relative humidity of the analysis chamber was maintained until the sample mass percentage varies less than 0.0001% over a 5 min period or the step time exceeds 24 h. Thermogravimetric analyses (TGAs) were performed on a TGA 851e analyser (Mettler Toledo, Greifense, Switzerland). Experiments were carried out under a nitrogen flow (50 mL·min<sup>-1</sup>) from 25 °C to 800 °C at a heating rate of 10 °C·min<sup>-1</sup>. To avoid any interaction with the phosphorus derivatives, a sapphire crucible (70  $\mu$ L) was used. All experiments were performed in triplicate on free 50  $\mu$ m thick coating films. Characteristic data such as T<sub>5%</sub>, the temperature corresponding to 5% of degradation,  $T_{max}$ , the temperatures of the maximum degradation rates and the percentages of residues at 800 °C were determined.

#### 2.5. Characterisation of the Coating Adhesion on Wood

Adhesion was investigated using pull-off tests based on the test method described in the ASTM D4541-17 standard. Aluminium dollies with a diameter of 20 mm were glued on the coating using a two-component epoxy adhesive (Lepage Marine Epoxy, Henkel, Mississauga, ON, Canada). Prior to the glue application, the dolly surface was sanded with a P-150-grit paper and cleaned with a wipe. The same procedure was performed on the coating surface with a finer sanding paper (P-1500-grit). Steel hex nuts (79 g) were placed on dollies during the adhesive curing to ensure an even pressure applied on each sample. After 48 h, the test area around the dolly was scored by means of a dolly cutter, until the wood substrate was reached. This ensures testing the same surface area. Pull-off tests were carried out on a QTest/5 Elite electromechanical test system with a 5 kN load cell (MTS, Eden Prairie, MN, USA) at a 2 mm·min<sup>-1</sup> pull rate. The coating tensile strength was calculated according to Equation (4), where  $F_{max}$  corresponds to the load at fracture (N) and d, to the dolly diameter (mm). Fracture type was visually assessed based on the described method in the ISO 4624:2016 standard. Twenty repetitions per formulation were performed.

$$\sigma = \frac{4F_{max}}{\pi d^2} \tag{4}$$

The statistical analysis of data was achieved on the software R: a language and environment for statistical (R Foundation for Statistical Computing, Vienna, Austria). Prior to analysis, the normal distribution of residuals was examined as well as the homogeneity of variances to ensure the validity of the analysis. One-way ANOVA was executed to compare the impact of phosphorus monomer addition in the coating formulations on the pull-off strength. The Tukey's HSD test allowed a pairwise comparison between the group to identify significant differences at a 0.05 level.

# 2.6. Fire Performance of Coated Wood Samples

The fire behaviour of the treated wood samples was assessed on a dual cone calorimeter (Fire Testing Technology, East Grinstead, UK). Cone calorimeter is a bench-scale test method widely used to assess a material's fire behaviour. It gives different parameters as the heat release rate, the time to ignition or the mass loss of the combusting material. However, it offers a limited interpretation of a fire scenario as it does not consider flame spreading.

Experiments were carried out on  $100 \times 100$  mm samples placed in the horizontal position. The distance between the sample and the cone heater was set at 25 mm. Heat flux was set at 35 kW·m<sup>-2</sup> for the cone calorimeter tests, corresponding to an early developing fire scenario. Such a heat flux is recommended for explanatory testing [29]. It is particularly appropriate to assess flame-retarded polymers as it matches the fire stage in which their action is crucial. Ignition was forced and the test was stopped 120 s after flame extinction. Wood sample backsides were wrapped in aluminium foil before being put in the sample holder. All experiments were performed in quadruplicate. In order to characterise the fire behaviour of the sample, the following data were gathered: the average time to ignition (TTI), the average peak of the heat release rate (pHRR) and the average total heat released (THR).

Cone calorimeter residues were collected and characterised with an Inspect F50 SEM equipped with a field emission gun source (FEI, Hillsboro, OR, USA). Elemental analysis on the residues was performed by means of energy dispersive spectroscopy (Octane Super-A, EDAX-AMETEK, Mahwah, NJ, USA). The acceleration voltage was set at 15 kV. Prior to analysis, all samples were covered with a conductive Au/Pd deposit.

#### 3. Results

#### 3.1. Photopolymerisation

DSC analysis assesses the heat flow of a material as a function of time and temperature compared to a reference. When coupled with a UV lamp, it enables the measurement of

different parameters specific to photo-curable systems. Photo-DSC results are presented in Figure 2 and Table 2.



Figure 2. Polymerisation rate of the different coatings.

**Table 2.** Coating viscosity and photo-DSC results including the induction time, the maximum heat flow, the rate of polymerisation and the unsaturation conversion.

Formulation	Viscosity (cP, 23 °C)	t <sub>ind</sub> (s)	<i>H<sub>max</sub></i> (W.g <sup>-1</sup> )	$Rp^{max}$ (s <sup>-1</sup> )	%Conversion (%)
F0	630	$1.06\pm0.04$	$58\pm2$	$16.1\pm0.4$	$68\pm3$
F1	840	$1.10\pm0.02$	$60 \pm 1$	$16.1\pm0.4$	$69\pm1$
F2	1230	$1.13\pm0.01$	$60\pm3$	$15.3\pm0.7$	$67\pm2$

All the rates of polymerisation curves demonstrated a steep increase within a few seconds after the beginning of the irradiation. Then, a rapid decrease in the rate of polymerisation was observed. Such a heat flow or a *Rp* behaviour was already reported in the literature for the free radical polymerisation of acrylate systems [30,31]. The rate of polymerisation of free radical polymerisation can be divided into different steps. The induction period is followed by the autoacceleration step, also called the Trommsdorff gel effect or the Norrish–Smith effect. *Rp* drastically increases due to the increasing viscosity of the polymerising system that slows termination reactions [32]. After reaching its maximum, Rp diminishes during the phase of autodeceleration. The propagation is then controlled through diffusion [33]. In this study,  $Rp^{max}$  were in the same range, with a value of 15.3 s<sup>-1</sup> for F2 and 16.1 s<sup>-1</sup> for the other systems. The conversion percentages were close to 70% for all coating formulations. The conversion percentages being kept in the same range when replacing the TPGDA by the phosphorus monomer demonstrated its active participation in the curing reaction. Thus, TAEP was successfully incorporated in the polymeric network created during the photopolymerisation of F1 and F2 coatings. No major difference in the induction time nor in the maximum heat flow,  $H_{max}$ , was noticed.

In the literature, a sharp peak in the rate of photopolymerisation was also observed for TAEP containing formulations [34,35]. However,  $Rp^{max}$  varied with the phosphorus monomer content. Tests were performed at 2.4 mW.cm<sup>-2</sup> or at a lower irradiance, greatly inferior to the 50 mW.cm<sup>-2</sup> used in this study. Such an irradiance was chosen so as to be more realistic to assess the photopolymerisation behaviour for an industrial application. Lower irradiance generates less energy, and hence, the polymerisation rate is slower. Moreover, the gelation effect induced by the trifunctional monomer addition in the system is greater, explaining the difference in the  $Rp^{max}$  value. The literature also reports that *Rp* tends to increase when the formulation viscosity decreases [36]. The viscosity is an important parameter for UV-curable systems as it affects different properties such as the ease of application, levelling, polymerisation rate and adhesion. In the present study, the viscosity varied significantly between the formulations (Table 2). However, the addition of TAEP, a non-linear phosphorus monomer, even at a high percentage in the formulation, did not affect the UV-curing behaviour.

#### 3.2. Coating Properties

# 3.2.1. Optical Transparency

Achieving transparency is an important parameter for wood coatings as they are often designed to protect the substrates while keeping their natural aspect. Film transparency was assessed by spectrophotometry on the visible spectrum, between 400 and 800 nm (Figure 3). F0 film was transparent with an 88% transmittance at 600 nm. With the addition of the FR monomer, the F1 and the F2 coatings also exhibited good optical transparency with a transmittance higher than 87% at 600 nm. All coatings preserved wood aspect as shown on Figure S3 in the supplementary information.



Figure 3. UV–Vis transmittance spectra of the coating film.

#### 3.2.2. Coating Mechanical Properties

All the factors impacting the chain mobility, such as the steric hindrance, the polymer functionality, the nature of the moving segment or the free volume available for motion, will affect the glass transition temperature. Both monomers added in the formulations in this study, TPGDA and TAEP, differ in their backbone structures and their number of acrylate functionalities. Such differences in chemical composition may lead to polymers exhibiting different T<sub>g</sub> and crosslinking densities [37].

DMA results are displayed in Figure 4; the storage modulus (E') and the tan  $\delta$  curves are shown in Figure S4 of the supplementary information. The glass transition temperature increased along with TAEP loading. T<sub>g</sub> reached 75 °C for F2, ten degrees higher than the one of F0. The oligomer supplier indicates a T<sub>g</sub> at 51 °C, measured by DSC. The T<sub>g</sub> of the TAEP homopolymer is also known (105 °C) as it has already been measured and reported in the literature [34,35]. While the value of T<sub>g</sub> increased with the phosphorus monomer percentage in the formulation, the crosslinking densities were in the same range. Given the standard deviation, the crosslinking densities were not considered to be different. The width of the tan  $\delta$  curves remained constant, evidencing good miscibility between the phosphate monomer and the acrylate monomer, TPGDA, and the epoxy acrylate oligomer.



Figure 4. Crosslinking density and glass transition temperature of the coatings.

Hardness refers to an imprecise term since its definition varies in the literature [38]. A broad definition of the surface hardness corresponds to the coating resistance to deformation by means of the indentation or the penetration of a solid object [39,40]. This is the reason why two technics (pendulum and indentation) were used in this study to determine the hardness of the coatings. The results are reported in Figure 5.



Figure 5. Pendulum hardness and indentation results of the coating films.

The pendulum hardness results exhibited a higher damping property for the coatings containing the phosphorus monomer. The F0 film reached 108 oscillations, while F1 and F2 achieved 89 and 78 oscillations, respectively. Replacing TPGDA by the TAEP monomer led to a change in the viscoelastic properties of the coating. The phosphorus-containing films were able to dissipate the pendulum energy of motion more easily.

Indentation hardness quantifies the coating film ability to resist to the penetration of an indenter. Preliminary tests confirmed that the maximum applied load ensured that the penetration was restricted to the upper part of the coating film. Having an optimal penetration depth guarantees a minimised influence of the substrate mechanical property on the results. The coating film containing only the acrylate monomer attained an instrumented hardness of approximately 65 MPa. With the addition of phosphorus monomer, the capacity to withstand penetration distinctly dropped under 45 MPa for both F1 and F2 formulations. The reduced elastic modulus  $E_r$  also followed the same trend, decreasing with a higher phosphorus content. Even though the conversion rate as well as the crosslinking density were not affected by the phosphorus monomer addition, a change in mechanical properties was observed. While TAEP had a higher functionality, the presence of the P-monomer brought flexibility to the coating films. The presence of water in the P-containing films was evidenced by further tests. The plasticising effect of the trapped water in the coating film is one possible explanation for their increased flexibility.

#### 3.2.3. Coating Water Sorption

Using phosphorus-containing polymers in a coating may cause some concern. Phosphorus polymers could be sensitive to moisture and in particular, P-O-C linkages present hydrolytic instability [41]. In order to assess the coating water affinity, Karl Fischer titration and dynamic vapour sorption experiments (DVS) measurements (Figure 6) were performed.



**Figure 6.** Karl Fischer titration results and, sorption and desorption curves of the coating films. The hollow circles correspond to the sorption step while the filled circles correspond to the desorption one.

Karl Fischer titration quantifies both free and bound water present in the coating film. The coating without P-monomer contained 0.82% of residual water. The water content rose with the phosphorus addition to achieve 1.30% for F2 coating. These results were consistent with the early stage TGA measurements (Figure 7) showing a higher mass decrease for the phosphorus-containing films. This gap in mass loss could be explained by their higher water content released below 150 °C.

DVS measures the quantity of water absorbed by the coating film in a given range of vapour concentrations. For the F0 film, water absorption was limited, and the mass gain reached 1.90% at the highest RH. The F2 sorption isotherm showed a steep increase in high-relative-humidity percentages. Such behaviour, corresponding to a low intake at low pressures followed by an increased in the high pressures, is typical of a Type III isotherm defined in the International Union of Pure and Applied Chemistry nomenclature [42]. F1 displayed a similar water uptake profile to a minor extent, as the mass change at the maximum RH reached 5.98% instead of 15.3% for F2. The F2 desorption isotherm did not return to a null mass change at a 0% RH. The hypothesis was made that the water is still present in the sample. Further energy seemed to be necessary to remove the bound water. This latter was removed prior to the DVS test by heating during the drying stage at 100 °C. F0 showed no hysteresis on the isotherms of sorption and desorption unlike the

coating samples containing phosphorus. The mechanism of water uptake was changed with the presence of a P-monomer in the coating. The absence of hysteresis suggested a plausible surface adsorption mechanism with limited to no bulk absorption. Hence, the results displayed the influence of adding phosphorus derivatives on the water uptake of coating films, mainly in the high RH range.



**Figure 7.** Curves of the thermogravimetric analysis performed under nitrogen and their derivatives for the TAEP monomer and the coating films with different phosphorus contents.

Although those results could appear as a limit for a coating application, the formulated coatings developed in this study are meant for a sealer use. In a complete wood finishing system, they would benefit from a topcoat applied above. This upper protective layer will limit water exchange and would be designed to resist abrasion and scratch. Once integrated in the finishing system, the sealer has a limited contribution to the surface hardness. Further investigations were thus performed on the coatings and the thermal stability was first studied.

# 3.2.4. Coating Thermogravimetric Analysis

The thermal stability of the coating films as well as the TAEP monomer was investigated by thermogravimetric analysis in an inert atmosphere. The mass loss curves and their derivatives are shown in Figure 7. The main results ( $T_{5\%}$ ,  $T_{max}$  and the percentages of residues at 800 °C) are featured in Table 3.

**Table 3.** Results of thermogravimetric analysis.  $T_{5\%}$  corresponds to the temperature at which 5% of the sample mass is lost,  $T_{max 1}$ ,  $T_{max 2}$  and  $T_{max 3}$  are the temperatures of the degradation rate maxima.

Formulation	T₅% (°C)	T <sub>max 1</sub> (°C)	T <sub>max 2</sub> (°C)	T <sub>max 3</sub> (°C)	Residue at 800 °C (%)
F0	295	158	371	418	$1\pm 1$
F1	196	161	357	424	$14.7\pm0.5$
F2	169	168	331	424	$19.6\pm0.5$
TAEP	113	132	307	436	$30.6\pm0.2$

The thermal decomposition of the pure monomer TAEP happened in three distinct steps, with maximum degradation rates at approximately 160 °C, 370 °C and 420 °C. A similar behaviour was reported in the literature for the thermogravimetric analysis of TAEP homopolymer in air [26]. Three main decomposition steps were described and assigned to the decomposition of the phosphate groups (from 160 °C to 270 °C), the decomposition of the ester groups (at approximately 330 °C) followed by the decomposition

of unstable structures in the char (above 500 °C). In our study, the analyses showed that the pristine coating underwent a three-stage decomposition process, with a first step around 160 °C, and then two overlapping steps between 300 °C and 475 °C. Even though the F0 formulation was more thermally stable under 400 °C compared to F1 and F2, there was no residue at 800 °C. The major F0 degradation range corresponded to a weight loss of approximately 90%, a percentage greatly higher compared to the ones of phosphorus-containing formulations. F1 and F2 coatings also displayed a several stages of decomposition but with better distinguishable steps. F1 coating first had thermal degradation at a higher temperature range followed by another thermal degradation at approximately 420 °C, which corresponds to the final decomposition of the oligomer and the monomer. For both phosphorus-containing coatings, it was observed that the thermal pyrolysis of unstable structures allowed the formation of a stable char above 450 °C. The major mass loss of F2 cured films occurred between 300 °C and 360 °C. The percentage of residue at 800 °C reached 14.7% for F1 and 19.6% for F2.

Thus, adding phosphorus compounds in the formulation shifts the thermal degradation to a lower temperature but leads to the formation of stable residues at 800 °C. The development of a char could be a benefit in terms of fire performance; the formation of such a protective layer was verified with the cone calorimeter tests.

## 3.3. Coating Adhesion on Wood

Good adhesion between the coating and the wooden substrate is mandatory to ensure good coating properties and durability [39]. Pull-off tests is a common method to assess the coating adhesion to the substrate that provides a quantitative result. The results of the pulloff strength of the different coatings applied on wood are presented in Figure 8. During the tests, only adhesive failure between the substrate and the first coat happened. An increasing phosphorus content in the coating led to an increasing fibre deposit on the dollies after the test. Thus, the cohesive strength of the coatings was good and the phosphorus coatings seemed to offer a better mechanical anchoring with a higher-wood fibres wetting. The adhesion strength also varied with the phosphorus content. Indeed, while the mean value of the adhesion strength of the F0 coating was under 1.00 MPa, it attained 1.01 and 1.12 MPa for F1 and F2, respectively. The statistical analysis conducted on the results revealed a significant difference in adhesion strength between the coating without phosphorus monomer and the one with the highest content. Thus, above a certain P-monomer addition in the formulation, the pull-off strength was slightly enhanced. Phosphorus derivatives are well-known adhesion promoters [43]. For instance, Maege et al. studied the adsorption of phosphorus derivatives on metallic substrates as an anchor to the coating system, offering an improved adhesion [44]. Wang et al. suggested that a phytic acid-based compound enhanced the adhesion of UV-curing coating to metal by the formation of P-O-Fe chemical bonds [45]. Even though the presence of phosphorus additives enhancing the adhesion with wood for coatings or adhesives has been reported in different studies [15,46,47], the mechanism explaining this improvement is not well detailed.

The difference in pull-off test results could be explained by several factors including the limited coating penetration into wood [48] or the UV coating shrinkage through curing [49]. During the photopolymerisation of acrylate systems, the weak intermolecular Van der Waals interactions in the liquid coating are replaced by strong and short covalent bonds between the carbon atoms in the solid film [50]. The distance between carbon atoms is reduced, building up internal stress in the coating. The volume contraction induces a shrinkage that may lead to low coating adhesion and poor mechanical properties [49]. In order to obtain a better understanding, SEM analyses were performed on the sample crosssections to observe the wood/coating interface (Figure 9). The F0 sample clearly displayed the coating detachment from the wooden substrate in different areas. The interface between the phosphorus coating and wood showed better bonding. The TAEP presence in the formulation seemed to induce lesser coating shrinkage through photopolymerisation, enhancing the coating adhesion.



**Figure 8.** Pull-off strength of the coatings applied on wood. Letters above the bars correspond to the groups determined in the Tukey comparison test after the ANOVA analysis ( $\alpha = 0.05$ ). Groups having a letter in common are not significantly different.





**Figure 9.** SEM images of the wood/coating interface, F0 (**a**), F1 (**b**) and F2 (**c**). Arrows show coating detachments of few microns wide from wood.

## 3.4. Fire Performance of the Coated Wood Samples

Heat release curves are displayed in Figure 10 and key values are summarised in Table 4. All coated panels present a heat release curve with two peaks, similar to what is usually observed in the literature for virgin wood [51]. The first peak is attained before charring. The heat release rate then decreases as a protective layer, i.e. a char, is formed. Then, the HRR curve illustrates the gradual burning through the thickness of the wood sample after the formation of the initial char. Once the carbonaceous protective layer crakes, a second HRR rise happens. The second peak also corresponds to the increased rate of volatile formation prior to the end of the flame burning [52].



Figure 10. Cone calorimeter heat release rate curves of the coated wood samples.

Table 4. Main	n cone calorime	ter results of the	he coated woo	od samples.

F0	<b>F1</b>	F2
0.0	1.7	3.4
$71\pm2$	$77\pm9$	$90\pm20$
$390\pm10$	$340\pm10$	$340\pm10$
$47\pm1$	$44\pm 2$	$42\pm1$
$7.6\pm0.3$	$9.8\pm0.6$	$10.4\pm0.6$
	F0 $0.0$ $71 \pm 2$ $390 \pm 10$ $47 \pm 1$ $7.6 \pm 0.3$	F0F1 $0.0$ $1.7$ $71 \pm 2$ $77 \pm 9$ $390 \pm 10$ $340 \pm 10$ $47 \pm 1$ $44 \pm 2$ $7.6 \pm 0.3$ $9.8 \pm 0.6$

\* Phosphorus coating contents were calculated based on the phosphorus content value (7.89 wt%) of the TAEP monomer obtained by ICP-OES analysis.

F0 coating cracked within a few seconds after exposure to the heat flux. The coating delaminated from the surface, exposing the wooden substrate to the flame. A high first heat release rate peak was rapidly reached for the F0 sample. A second peak was observed attaining a value of 390 kW·m<sup>-2</sup>. The higher the value of the HHR first peak for the F0 coating compared to the other samples was attributed to the greater organic coating contribution to the burning. The phosphorus coatings also showed some delamination but to a lesser extent compared to F0. This difference in coating adhesion to wood was already highlighted with pull-off tests. A good coating adhesion is critical in the beginning of the cone calorimeter test and decisive for the fire behaviour of the material. Some cracks also appeared on F1 and F2 coating surface after the ignition. Similarly to what was observed for the F0 coating, the HRR curve of F1-coated wood samples presented a first peak but with a lower value, suggesting the formation of a protective char layer.

The heat transfer and fuel supply to the flame were limited, slowing down the pyrolysis process. Cracks in the protective layer appeared, allowing the flame to reach the virgin wood. An increase in the pyrolysis then occurred, leading to a second heat release rate rise. For the highest phosphorus-FR-containing film (F2 coating), the curve depression was considerably flattened. It was assumed that the protective layer is formed more efficiently for the F2 sample as a plateau rather than a peak was observed on the HRR curve in the early stage of the test. In the case of phosphorus-containing coatings, the pHRR only reached 340 kW·m<sup>-2</sup> and was delayed compared to F0. Adding a phosphorus monomer enhanced the residual mass percentage as well as reduced the THR, suggesting an improved wood charring behaviour. The time to ignition also varied with the FR loading with an upward tendency.

A reduction of 13% in the pHRR could appear as a moderate improvement. However, adding a phosphorus monomer positively affected other parameters such as the percentage of residues after the test. Wang et al. also reported a pHRR decrease of approximately 10% with their best treatment obtained in the cone calorimeter test performed at 50 kW $\cdot$ m<sup>-2</sup> [15]. The wood coatings reported in this study contained the following FR at different ratios: a multifunctional bio-mercaptan of castor oil grafted thiol, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane and an organic phosphorus compound. The UV-curable coating was applied at 180  $\mu$ m (versus 50  $\mu$ m in the present study) on 4 mm thick Chinese fir samples. The pHRR curve followed a reverse tendency compared to our study, with a higher first peak compared to the second one. Higher pHRR decreases were observed for a non UV-curable waterborne intumescent wood coating [53] or for coating applied on wood with a thicker layer [54]. For the first study, Song et al. obtained a clear pHRR decrease of approximately 40% and a delayed TTI compared to pure wood, a 4 mm thick poplar panel. All the pHRR of the samples treated with the different intumescent coatings ranged from 140 kW·m<sup>-2</sup> to 190 kW·m<sup>-2</sup> after the cone calorimeter test. In the second study, epoxy coatings were applied on a poplar wood sample at a 5 mm thick layer. The authors reported a pHRR reduction of 20% with the addition of a phosphaphenanthrene-containing epoxy co-curing agent in the coating formulation compared to the epoxy coating reference.

The cone calorimeter residues were collected and analysed to better comprehend the charring mechanism. SEM analyses were performed on the residues collected after the test to confirm the action of phosphate moieties in the condensed phase (Figure 11). The mass percentages of different elements obtained from the EDS analysis performed on the same residues are gathered in Table 5.

Analysis Area	C (wt%)	O (wt%)	P (wt%)	Ca (wt%)	Mg (wt%)	Mn (wt%)	K (wt%)
F0—Area 1	65.45	27.33	0.31	4.41	1.08	0.98	0.44
F0—Area 2	12.28	51.08	1.59	21.95	4.84	4.85	3.40
F1—Area 3	81.69	16.49	1.46	0.35	-	-	-
F1—Area 4	81.16	17.24	1.44	0.17	-	-	-
F2—Area 5	76.47	21.04	2.14	0.35	-	-	-
F2—Area 6	80.77	16.44	2.11	0.52	0.15	-	-

**Table 5.** Elemental composition analysis performed on different areas (identified on Figure 11) of thecone calorimeter residues.

F0 residues displayed a very fragile fibrous structure with no visible coating deposit. No charring was observed, only ashes were formed. It is similar to wood sample morphology after being exposed to a flame as reported in the literature [55]. On the contrary, the flame-retarded samples clearly displayed some wooden charred structure demonstrating that a protective mechanism occurred. For both F1 and F2 samples, high temperature-resisting residues of the coating were noticeable. In the case of the F1 sample, a partial delamination of the coating was observed, revealing a thick char underneath. This solid structure is present on the right-hand side of Figure 11b. Fractures in the F1 residues were

also visible. They went through the coating and the substrate. F2 residues also displayed a thick char formation. Almost no coating detachment was noticed but cracks were still observed. Interestingly, most of the cracks did not go through the substrate either. Indeed, Figure 11d revealed that most F2 coating fractures were protected by an underneath layer. The F2 burnt sample showed a surface morphology with hollowed areas and trapped bubbles underneath the top layer.



Figure 11. SEM images of cone calorimeter residues of F0 (a), F1 (b) and F2 (c,d).

Thus, the presence of a protective layer after the cone calorimetry tests on the residues of wood samples, either coated with F1 or F2 formulation, validates an action of the phosphate moieties in the condensed phase. The TAEP addition to the coating formulation helped the char formation, increasing the mass residue. An insulating barrier is formed, protecting the underneath substrate from fire, and preventing gas exchange between the condensed phase and the flame.

EDS analyses further endorsed the action of phosphorus compounds participating in the char formation. Whereas the analysis of the F0 residues revealed the presence of typical elements found in wood ash, the elemental composition significantly varied when a phosphorus-containing coating was applied on the wood. Misra et al. observed that the wood ash at 600 °C was mainly composed of calcium, potassium and magnesium, apart from carbon and oxygen elements [56]. Phosphorus, sulphur and manganese were also present to a minor extent. Wood decomposition forms calcium carbonate and oxide [57]. High O wt% and Ca wt% for F0 endorsed the presence of calcium derivatives. F1 and F2 surface analysis demonstrated higher C and P contents. The phosphorus coming from the FR coating application was still present in the residues after the cone calorimeter test. As expected, a higher P content was observed for F2 compared to F1. A significant amount of phosphorus induces an active role of the FR in a condensed phase mechanism. It is worth mentioning that even though the P content of area 2 of F0 sample and the one of F1 sample were in the same range, these were not comparable as the percentages of the other elements were completely different. EDS analysis gives the relative elemental composition of a local sample area based on the total detected elements in it. While F0 corresponded to an ashes area with a C content under 15%, the F1 sample charred, resulting in a high C content, above 80%.

We may conclude that a decrease in the pHRR combined with an increase in the residual mass indicates an effective action of the TAEP addition regarding flame retardancy. The cone calorimeter tests along with the observation of the residues also suggested a difference in coating adhesion depending on the phosphorus rate in the formulation. With a higher phosphorus content, the least coating delamination occurred, contributing to the improvement of the fire behaviour of the coated wood.

## 4. Conclusions

High-solid-content transparent UV-curable coatings were prepared at different TAEP percentages in an acrylate-based formulation. Coatings were applied on wood panels. The photopolymerisation kinetics was monitored by photo-DSC. It was shown that adding the phosphorus monomer did not impact the UV-curing behaviour as the conversion of the acrylate group was in the same range, i.e., over 65%. A change in coating hardness was observed and attributed to the fact that TAEP brought flexibility to the coating films. This study also showed that P-containing coatings displayed a higher water sorption for high relative humidity. The issue related to water affinity could be easily lowered by integrating the formulation as a sealer coat in a prefinished wood flooring system. The presence of the phosphorus monomer at the highest content significantly improved the coating adhesion on the wood. The wood coating fire efficacy was evaluated by cone calorimetry. A decreased pHRR as well as an enhanced residue percentage were obtained for all the phosphorus-containing coatings. SEM and EDS analyses performed on the collected residues confirmed the formation of a solid protective structure and the presence of phosphorus in the flame-retarded samples. The phosphorus FR had an effective action in the condensed phase, improving the fire retardancy of the coated wood. The formulation containing approximately 40% of TAEP clearly displayed the best FR performances compared to the non-FR coating. Furthermore, the major expected properties of a sealer coating were positively assessed. This study thus demonstrates the high potential of phosphorus-containing UV-curable acrylate system to improve the fire behaviour of wood flooring. Further investigations could include the introduction of another FR retardant in the formulation. Nitrogen or silicon compounds have demonstrated a synergistic behaviour along with the phosphorus FR. The F2 coating highlighted in this study could also be of interest for metal coating where TAEP could act as both a flame retardant and an adhesion promoter.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/coatings12121850/s1. Figure S1. <sup>1</sup>H NMR spectrum of tri(acryloyloxyethyl) phosphate (TAEP); Figure S2. FTIR spectrum of tri(acryloyloxyethyl) phosphate (TAEP); Figure S3. Appearance of the coatings applied on wood panels; Figure S4. Storage modulus and tan  $\delta$  curves resulting from DMA analysis on the coating films.

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