



HAL
open science

Enhancing Flame Retardancy of Flax Fabrics through Phytic Acid Grafting

Antoine Ishak, Claire Longuet, Belkacem Otazaghine, Rodolphe Sonnier

► **To cite this version:**

Antoine Ishak, Claire Longuet, Belkacem Otazaghine, Rodolphe Sonnier. Enhancing Flame Retardancy of Flax Fabrics through Phytic Acid Grafting. ACS Applied Polymer Materials, 2024, 6 (10), pp.5642-5652. 10.1021/acsapm.4c00198 . hal-04575634

HAL Id: hal-04575634

<https://imt-mines-ales.hal.science/hal-04575634v1>

Submitted on 10 Jun 2024

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

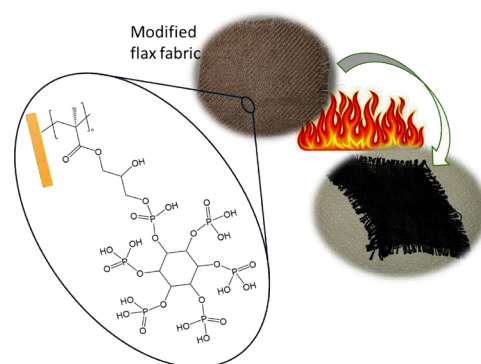
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Enhancing Flame Retardancy of Flax Fabrics through Phytic Acid Grafting

Antoine Ishak, Claire Longuet, Belkacem Otazaghine, and Rodolphe Sonnier*

ABSTRACT: Flame-retardant flax fabrics were developed using the grafting of phytic acid (PA) through a two-step process. First, flax fabrics were functionalized with glycidyl groups employing the polymerization of glycidyl methacrylate (GMA) via a simultaneous e-beam irradiation procedure. Subsequently, the modified flax fabrics were treated with PA using two different techniques: the first method involved a direct grafting approach, where the phosphonic functions of PA reacted with the glycidyl groups. The second technique employed a coating process, which was based on a combination of PA and ethylene glycol diglycidyl (EGDG) as a curing agent, producing a phosphonated layer on the flax fibers. The treatment processes were applied to pristine and alkali pretreated flax fabrics, allowing an investigation into the impact of delignification and PA grafting on burning behavior. SEM-EDS, ^{13}C and ^{31}P solid NMR, and FTIR were used to characterize the treatment process steps. Thermogravimetric analysis (TGA), pyrolysis combustion flow calorimetry (PCFC), and cone calorimetry tests were performed to evaluate the pyrolysis and combustion behaviors of prepared samples. The treated flax fabrics exhibited a good flame-retardant property only at 1.3 wt % of P content, while for a lower content, it was not effective enough. Moreover, the delignification of the flax fabric contributed significantly to enhance its fire behavior.

KEYWORDS: flax fabrics, phytic acid (PA), flame-retardant, e-beam irradiation, grafting/coating



1. INTRODUCTION

In recent years, the textile industry has seen a remarkable resurgence in the exploration of plant fibers, including cotton, flax, jute, and kenaf. This interest is primarily driven by an urgent need to address environmental and sustainability concerns which are related to the conventional textile production methods. Unlike synthetic alternatives, the natural fibers are renewable, in addition to their advantages such as availability, cost competitiveness, low density, and good mechanical properties.

Plant fibers offer exceptional properties that seamlessly align with the evolving ecological and economic imperatives of society.¹ However, plant fibers tend to exhibit limited resistance to ignition and rapid flame propagation when subjected to fire-related conditions, which is one of their drawbacks. This requires comprehensive research and development efforts in order to enhance the flame retardancy of plant fibers in textile applications.²⁻⁸

Several strategies have been proposed for the modification of plant fibers by grafting flame retardants (FRs) onto the fiber structure to reduce flammability such as UV irradiation,^{9,10} plasma treatment,¹¹ sol-gel treatment,¹² and e-beam irradiation.¹³⁻¹⁵ These strategies allow the creation of covalent bonds between the fiber structure and the FR molecules.

E-beam irradiation is used in the field of fiber surface modification due to its advantages, such as simplicity, reaction control, reasonable cost, and respect of the environment. Indeed, the reactions can efficiently take place through the direct injection of energy into the material, eliminating the need for initiators or catalysts.¹⁶

Many researchers have modified natural fibers by grafting polymers or copolymers onto their structure via e-beam irradiation. In this process, polymerization of monomers can be initiated by radical species formed during irradiation on fiber structures, producing grafted polymer chains.¹⁷ For example, Taibi et al.¹⁸ prepared flame-retardant flax fabrics via a preirradiation grafting process, where the fabrics were irradiated in a first step using an e-beam at different doses. Then, the activated fabrics were treated with dimethyl-(methacryloxy)methyl phosphonate (MAPC1) using water as a solvent. The phosphorus content in the treated fabrics varied between 2.2 and 7 wt % for doses ranging from 10 to 100 kGy.

Sonnier et al.¹³ and Hajj et al.¹⁹ prepared flame-retardant flax fabrics using MAPC1 and vinyl phosphonic acid (VPA), respectively, as flame-retardant monomers via simultaneous irradiation grafting process. Irradiation of the flax was done in the presence of monomers, and the radical species generated led to polymerization reactions into fibers.¹⁶ However, monomers that are synthetic molecules while using renewable and environmentally friendly phosphorus-based flame retardants are a preferable choice.

Numerous studies have focused on environmentally friendly flame retardants, especially biobased ones.²⁰ PA, which is a natural source of phosphorus, was highly investigated as a flame-retardant biomolecule.^{6,21–26}

Kang et al.²⁷ have prepared flame-retardant cotton fabric using PA via a layer-by-layer (LbL) assembly coating method. The treated fabrics displayed an effective flame retardancy with 41% reduction in the peak heat rate release (pHRR). Ehsanimehr et al.²⁵ also used PA to modify flax fabrics via the same method. The authors showed that values of pHRR of treated fabrics significantly decreased by about 77%. However, the LbL coating method faces some limitations, particularly when this technology is transferred from laboratory-scale to industrial-scale. Another drawback of the LbL method concerns the durability, as it generally depends on electrostatic interactions. This significantly reduces the lifetime of LbL flame-retardant coatings.²⁸ On the other hand, Feng et al.²⁹ prepared flame-retardant cotton fabric by grafting phosphorus ammonium phytate (PAP), producing P–O–C bonds with cotton fibers. The pHRR value for treated cotton decreased up to 10.7 kW/m² compared to 195.1 kW/m² for the pristine one. Furthermore, the effectiveness of PA as a flame-retardant biomolecule is confirmed by the successful preparation of a durable flame-retardant lyocell and hemp fibers by Liu et al.³⁰ and Antoun et al.,³¹ respectively, using the same method.

In the present work, another grafting method was proposed in order to prepare durable flame-retardant flax fabrics using PA via a two-step process. First, the fabrics underwent grafting with glycidyl methacrylate (GMA) polymer chains through a simultaneous e-beam irradiation procedure. This procedure was essential for introducing glycidyl groups into the flax fiber structure.³² Subsequently, by taking advantage of the chemical reaction between phosphate (P–OH) and glycidyl groups,^{33–35} the successful grafting of PA onto the fabrics was achieved with different phosphorus content rates. This process was applied directly on the pristine flax fabrics and again on delignified flax fabrics in order to investigate the influence of lignin on the flame retardancy.

SEM-EDS, ¹³C and ³¹P solid NMR, and FTIR were used to characterize the different steps of the treatment. TGA, PCFC, and cone calorimetry were performed to evaluate the pyrolysis and combustion behaviors of prepared samples.

2. MATERIALS AND METHODS

2.1. Materials. Glycidyl methacrylate, 97%, was supplied by ABCR. PA solution (50 wt % in water) and ethylene glycol diglycidyl ether were purchased from Sigma-Aldrich. Ethanol and sodium hydroxide (NaOH) were obtained from PanReac AppliChem. All these chemical products were used without further purification. Flax fabric (200 g/m²) was supplied by Hexcel (France) and contains about 81 wt % of cellulose, 13 wt % of hemicellulose, and 2.7 wt % of lignin.

2.2. General Procedure for the Preparation of Glycidyl Grafted Flax Fabrics. Two grams of pristine flax fabric (F^{prist}), corresponding to a piece of about 10 × 10 cm², were rolled up and

introduced into a polyethylene tube (Figure S1). Then, the tube was filled with a GMA solution using a water/ethanol (1/4) (w/w) solvent mixture. The tube was irradiated with an e-beam at room temperature by Ionisos SA (Chaumesnil, France). Several samples using different concentrations of GMA and different doses of radiation were prepared for this study (Table 1). Finally, the fabric

Table 1. Samples of Grafted Flax Fabric with GMA under Different Conditions

N°	type of sample	GMA concentration solution (mol/L)	irradiation dose (kGy)	grafting rate (wt %)
1	F ^{prist}	1	10	15
2	F ^{prist}	1	50	34
3	F ^{prist}	1	100	40
4	F ^{prist}	0.5	10	6
5	F ^{prist}	1.5	10	20
6	F ^{prist}	2	10	30
7	F ^{Alk}	0.5	10	9
8	F ^{Alk}	1	10	22
9	F ^{Alk}	1.5	10	30

samples were taken out of the tubes, squeezed with papers, washed by the water/ethanol mixture 3 times using ultrasound, and dried in the oven at 60 °C for 1 h. The obtained fabric in this step was noted (F^{prist}/GMA).

In this process, polyglycidyl methacrylate chains will be grafted simultaneously on the flax fibers. This allows the generation of reactive glycidyl groups on the fiber surface, which will react with PA later and covalently bind it to the fiber.

Other samples were prepared in the same way, but first they were pretreated with an alkaline solution as follows: 2 g of pristine flax, corresponding to a piece of about 10 × 10 cm², was dipped into 200 mL of NaOH solution (0.5 M) at 70 °C for 3 h under stirring. Then, a neutralization process was performed with 200 mL of acetic acid (0.6 M) for 30 min at 70 °C followed by washing with deionized water to remove all acetic acid traces and drying for 1 h at 60 °C. This treatment aims to remove lignin from flax fabrics. The obtained fabric in this step is called F^{Alk}. Afterward, the delignified fabric was grafted by GMA using the same method; the obtained fabric in this case is called F^{Alk}/GMA.

The mass gain of the samples was calculated as follows:

$$\text{weight gain} = 100 \times \frac{(\text{final fabric weight} - \text{starting fabric weight})}{\text{final fabric weight}}$$

This value represents the grafting rate of GMA for the modified sample.

2.3. General Procedure for the Grafting of PA onto Epoxy Functionalized Flax Fabrics. Six grams of PA solution were placed into a bottom flask of 25 mL and diluted by 9 g of water. The prepared solution was adjusted to pH = 2 using sodium hydroxide (1 M) to avoid damaging the fabric. Then, 0.3 g of F^{prist}/GMA was introduced into this solution and stirred for 2 h at 80 °C. In this step, the grafted glycidyl groups on the fabric react with the P–OH groups of PA. However, a part of the glycidyl groups is hydrolyzed during this step (Figure 1). The fabric was taken out, squeezed with absorbent papers, and washed twice with deionized water at 80 °C to remove the ungrafted PA, followed by drying at 60 °C in an oven for 1 h. The obtained fabric in this step is called F^{prist}/GMA-PA. The same process was applied on F^{Alk}/GMA in order to prepare F^{Alk}/GMA-PA.

2.4. Coating of Phytic Acid onto Glycidyl Grafted Flax Fabrics. Three grams of PA solution (50 wt %) were placed into a bottom flask of 25 mL. Then 2 g of ethylene glycol diglycidyl ether (EGDE) was dissolved in 7 g of ethanol and added to the solution with stirring until completely homogenized. Next, 0.3 g of F^{prist}/GMA was immersed in the solution for 5 min. Then, the fabric was taken out and cured in an oven at 80 °C for 1 h. Afterward, the fabric was squeezed with papers and washed 3 times with ethanol, followed by

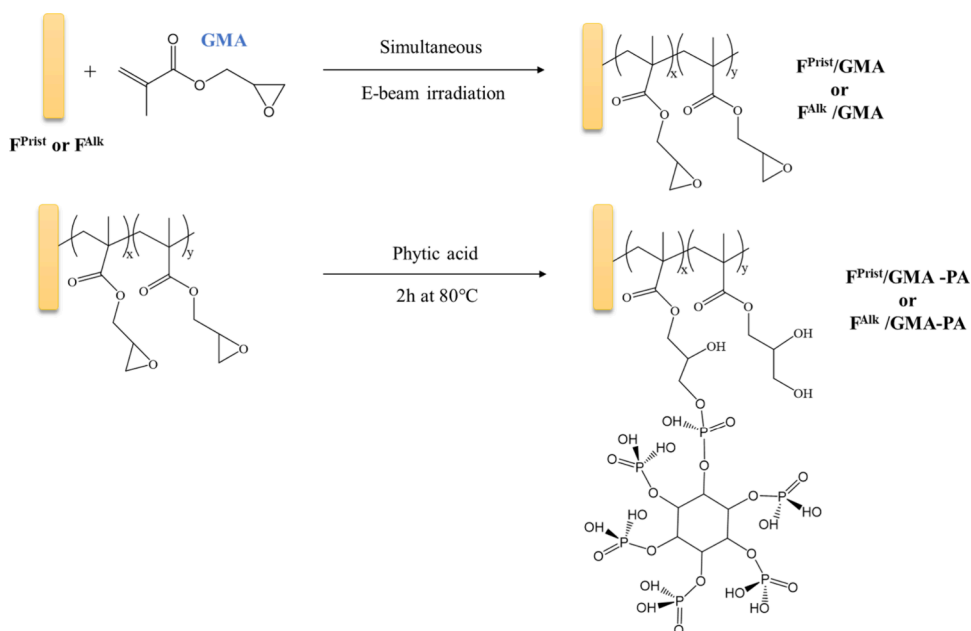


Figure 1. Schematic representation of the flax fabric treatment: GMA radio-grafting via a simultaneous e-beam irradiation procedure followed by PA treatment.

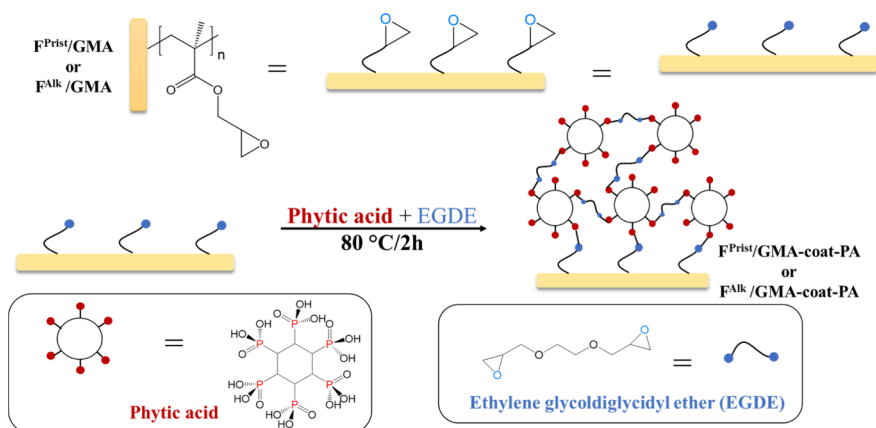


Figure 2. Schematic representation of the coating treatment of flax fabrics: GMA radio-grafting via a simultaneous e-beam irradiation procedure followed by the coating of PA/EGDE.

evaporation of the solvent at 60 °C in an oven for 1 h (Figure 2). Finally, the fabric was washed 3 times by ethanol to remove all unreacted molecules. During this process, the reaction of glycidyl groups present on the fiber surface allows the coating layer to be fixed to the flax structure. The obtained fabric in this step is called F^{Prist}/GMA-coat-PA. The same process was applied on F^{Alk}/GMA in order to prepare F^{Alk}/GMA-coat-PA.

2.5. Measurements. **2.5.1. Fourier Transform Infrared Spectroscopy (FTIR).** Fourier transform infrared spectra were obtained using a Bruker VERTEX 70 spectrometer used in attenuated total reflectance mode by performing 32 scans between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

2.5.2. ¹³C and ³¹P Solid State NMR. After being cut to small pieces (1 × 1 mm²), fabric samples were analyzed by nuclear magnetic resonance (NMR) spectroscopy in order to verify the reaction of the glycidyl groups as well as the grafting of PA on the fabrics.

The ¹³C solid state NMR spectra were recorded on a VARIAN VNMRS300 spectrometer at 300 MHz (“Wide Bore” magnet of 7.05 T). A VARIAN T3MAS (Magic Angle Spinning) probe was used with 7.5 mm ZrO₂ rotors. The measurements were carried out using the Single Pulse quantitative technique, with 1H decoupling. We used a $\pi/2$ pulse of 5 μ s with a recycling time of 600 s. The samples were run

at a speed of 5 kHz. The chemical shift value was calibrated using a secondary reference of adamantane, the left signal of which was set at 38.50 ppm. The acquisition window and the filtering were 50 and 30 kHz, respectively.

The solid state NMR spectrum of ³¹P was recorded on a VARIAN VNMRS400 spectrometer at 400 MHz (9.4 T “Wide Bore” magnet). A VARIAN T3MAS (Magic Angle Spinning) probe was used with 3.2 mm ZrO₂ rotors. The measurement was carried out with the Single Pulse quantitative technique, with 1H decoupling. We used a $\pi/2$ pulse of 4 μ s with a recycling time of 100 s. The sample was rotated at a speed of 20 kHz. The chemical shift value was calibrated using a secondary reference of monobasic potassium phosphate (KH₂PO₄), whose left signal was set at 4.1 ppm. The acquisition window and the filtering were 250 and 50 kHz, respectively.

2.5.3. Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES). ICP-AES analysis was performed in order to determine the phosphorus content in treated fabric samples.

First, 50 mg of the sample was mineralized by a nitrating mixture (nitric acid/sulfuric acid) with a 1/2 volume ratio using microwave oven (MILESTONE 1200-MEGA) as a heat source. The microwave is programmable for the power in four discrete steps with five power

settings (ranging from 250 to 750 W), a heating time of 20 min, and a cooling time of 4 h.

Afterward, the mineralized sample was diluted with deionized water, filtered, and analyzed by a HORIBA Jobin Yvon–Activa M spectrometer using a phosphorus calibration curve of 0–5–25–100 mg/L and a phosphorus peak detection wavelength of 213 nm.

2.5.4. Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectrometry (SEM-EDS). The cross section of fabrics was analyzed via a scanning electron microscope (FEI Quanta 200). The samples were placed on a vertical sample holder after being cut with a single edge blade. The scanning was performed under high vacuum at a voltage of 12.5 kV and a working distance of 10 mm. To locate the presence of the phosphorus element which represents the grafted PA into fabric, SEM analysis was coupled with an energy dispersive X-ray spectroscopy, EDS, instrument (Oxford INCA Energy system).

2.5.5. Thermogravimetric Analysis (TGA). A thermogravimetric analyzer (Setaram Setsys) was used for studying the thermal decomposition of the fabrics. First, 10 ± 1 mg of the sample was heated in alumina ceramic crucibles from 30 to 900 °C (heating rate of 10 °C/min) under inert atmosphere (N_2 , 40 mL/min). During the analysis, 15 min of isotherm at 100 °C was done in order to remove adsorbed water and facilitate the comparison between samples.

2.5.6. Pyrolysis Combustion Flow Calorimetry (PCFC). To evaluate the fire behavior of fabric samples at the microscale, a pyrolysis combustion flow calorimeter (Fire Testing Technology, Ltd., UK) was used. Samples (2–4 mg) were pyrolyzed under nitrogen (100 mL/min) at a heating rate of 1 °C/s from 100 to 750 °C (anaerobic pyrolysis—method A according to the standard ASTM D7309). After the pyrolysis, gases were fully oxidized in the presence of a N_2/O_2 (80/20) mixture. Huggett’s equation was applied to calculate the heat rate release (HRR) (1 kg of consumed oxygen is equivalent to 13.1 MJ of released energy). Each test was performed twice to confirm the repeatability of the results. The peak heat rate release (pHRR), the temperature at pHRR (T_{max}), the total heat release (THR), the heat of complete combustion (HCC), and the residual char were determined.

2.5.7. Cone Calorimetry. The fire behavior of fabrics at the bench scale was evaluated using the cone calorimetry test. This experiment was performed to evaluate the effect of PA on the fabrics. The 10×10 cm² sample is placed horizontally on a sample holder keeping 25 mm distance between the radiant cone and the sample, which is surrounded by aluminum foil. The bottom surface is insulated with rock wool. Air flow is fixed at 24 L/s and the heat flux was adjusted at 35 kW/m². A metal grid is placed on the sample during the test in order to avoid the deformation of the fabric. The samples decompose and release combustible gases, which ignite in the presence of a spark. The heat release rate (HRR) is calculated according to Huggett’s relation (Huggett, 1980). The peak heat release rate (pHRR), total heat released (THR), effective heat of combustion (EHC), and final residue content are determined.

3. RESULTS AND DISCUSSION

3.1. Characterization of Modified Fabrics with GMA.

The influence of the GMA concentration as well as the irradiation dose on the mass gain of the pristine fabrics was studied. As shown in Figure 3 and Table 1, the more the irradiation dose increases, the more the mass gain increases for the same concentration of GMA (1 mol/L). However, since irradiation has adverse effects on textiles,³⁶ the dose of 10 kGy is the most preferred. In the same way, the more the concentration of GMA increases, the more the mass gain increases at the irradiation dose 10 kGy. These results show the possibility of easily controlling the grafting rate of GMA on flax fabric and of obtaining high grafting yield even at a low (safe) dose.

On the other hand, it is noteworthy that the delignification of flax fabric exhibits a perceptible impact on the weight gain

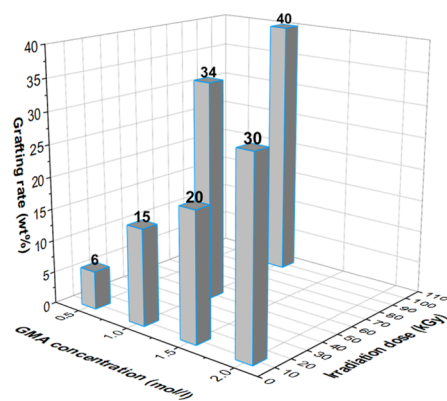


Figure 3. Grafting rate of GMA for pristine flax fabric according to the concentration of the solution and the irradiation dose.

observed for the radio-grafting step of GMA. When comparing delignified fabrics with their pristine ones under identical irradiation conditions and GMA concentrations, it becomes evident that the delignification process manifests a higher grafting rate. Indeed, at a 10 kGy irradiation dose, F^{Alk}/GMA has a greater weight gain than the F^{prist}/GMA .

As shown in Figure 4, when subjected to an e-beam irradiation dose of 10 kGy and immersed in a 1 mol/L solution

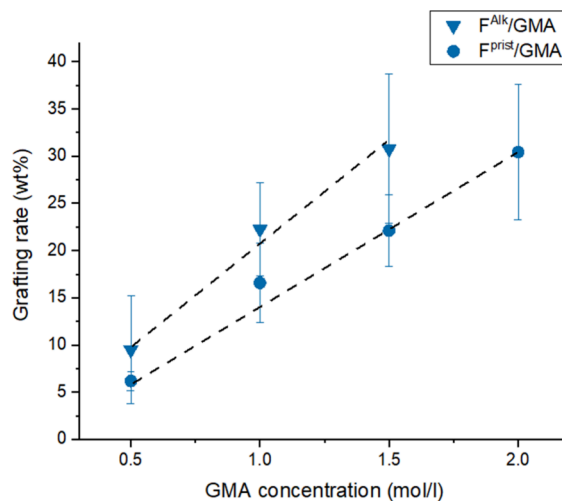


Figure 4. Grafting rates of GMA for pristine and delignified flax fabrics at a 10 kGy irradiation dose with different concentrations of GMA solution.

of GMA, the mass gain for F^{prist}/GMA is approximately 15 wt %, while the fabric subjected to delignification treatment (F^{Alk}/GMA) under the same conditions exhibits a notably higher weight gain of about 22 wt %. This divergence in weight gain becomes even more pronounced when the irradiation dose remains at 10 kGy and the GMA concentration is increased to 1.5 mol/L, resulting a 30 wt % weight gain for F^{Alk}/GMA and 20 wt % for F^{prist}/GMA . Briefly, an increase about 50% of weight gain is observed for the delignified fabric compared to pristine one at the same conditions whatever the GMA concentration.

Modified samples (with grafting rates of 15%, 20%, and 30%, which correspond to samples 01, 05, and 06, respectively) were analyzed using infrared spectroscopy to detect some modifications after grafting (Figure 5). First of all, there are

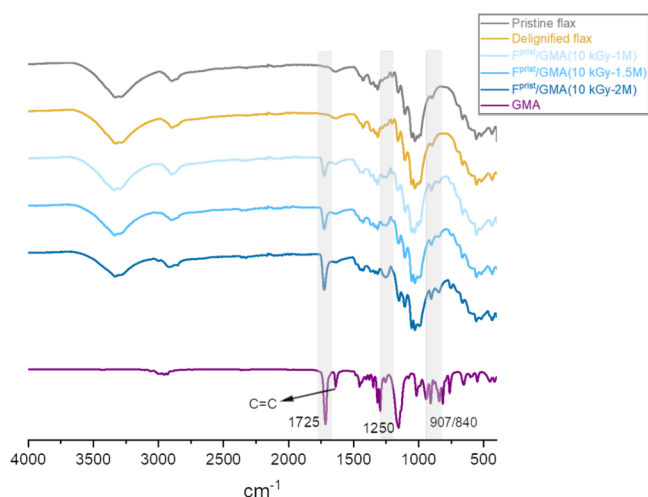


Figure 5. FTIR spectra of pristine and delignified flax and radio-grafted flax fabrics with several grafting rates.

no modifications in the spectrum of delignified flax compared to pristine flax. This is probably due to the low amount of lignin generally observed for flax fibers (approximately 2.7 wt %). On the other hand, after GMA treatment, the bands corresponding to the carbonyl group ($\text{C}=\text{O}$ at 1725 cm^{-1}), to the $\text{C}-\text{CH}_3$ group (at 1250 cm^{-1}), and to the glycidyl group (at 907 and 840 cm^{-1}) appear very clearly on the spectra of $\text{F}^{\text{Prist}}/\text{GMA}$ samples for grafting rates of 15, 20, and 30 wt %. Also, the intensity of these bands increases by increasing the weight gain due to the grafting. Furthermore, the band corresponding to the $\text{C}=\text{C}$ group at 1600 cm^{-1} of the methacrylate monomer is not observed, which proves the success of grafting GMA polymer chains onto flax fabrics.

3.2. Characterization of Fabrics Modified with PA by Grafting and Coating Methods. As demonstrated above, the grafting of flax fabric with GMA polymer chains is a fairly controlled process, enabling the preparation of $\text{F}^{\text{Prist}}/\text{GMA}$ and $\text{F}^{\text{Alk}}/\text{GMA}$ with high grafting rates even at low irradiation doses. Consequently, samples of pristine and delignified fabrics were prepared with similar GMA grafting rates (about 30 wt %) and subjected subsequently to modification with PA using

the grafting and coating methods. Finally, after these treatments, the phosphorus content of samples was measured by ICP-AES analysis, as shown in Table S1, to assess the efficiency of the two methods. These samples were then characterized to investigate their thermal behavior and flame-retardant properties. Both pristine and delignified fabrics exhibit the same phosphorus content for a given method (i.e., grafting or coating), with the amount of GMA being the same for all fabrics. This is evidence that the presence of lignin has no impact on the grafting efficiency of PA. This result will allow the comparison of the treated flax fabric in the presence and absence of lignin in order to investigate the effect of this component on the fire behavior of the treated fabrics. Furthermore, the phosphorus content obtained for the grafting method is low ($<1\text{ wt }%$). We assume that this is due to the hydrolysis reaction which occurs for one part of glycidyl groups during the grafting reaction, which reduces the amount of available epoxy functions to react with PA. The phosphorus content is higher when the coating method was used.

It is worth mentioning that another sample of $\text{F}^{\text{Alk}}/\text{GMA}$ with different grafting rates of GMA was grafted by PA. The P content increased proportionally to the GMA grafting rate (Figure S2). However, P content was very low ($<0.5\text{ wt }%$) for lower GMA rates than 30 wt %.

3.2.1. ^{13}C and ^{31}P NMR Analyses of Modified Flax Fabrics. The chemical shifts observed in the ^{13}C and ^{31}P NMR analyses for both the $\text{F}^{\text{Prist}}/\text{GMA}$ and $\text{F}^{\text{Prist}}/\text{GMA-PA}$ samples provide indications on the evolution of the reaction during the treatment process (Figure 6).

In the ^{13}C NMR spectrum of $\text{F}^{\text{Prist}}/\text{GMA}$, specific bands appear, notably the carbon signals associated with main functional groups. The signal of the carbonyl group is clearly observed at 178 ppm, while the methyl group exhibits a distinctive peak at 18 ppm. In addition, the signal corresponding to the carbons of the epoxy cycle is highlighted.

In contrast, the ^{13}C NMR spectrum of $\text{F}^{\text{Prist}}/\text{GMA-PA}$ presents a clear difference compared to that of $\text{F}^{\text{Prist}}/\text{GMA}$. Here, all carbon peaks observed for $\text{F}^{\text{Prist}}/\text{GMA-PA}$ remain present except for the carbon signal of the glycidyl group, which completely disappears. This absence supports the

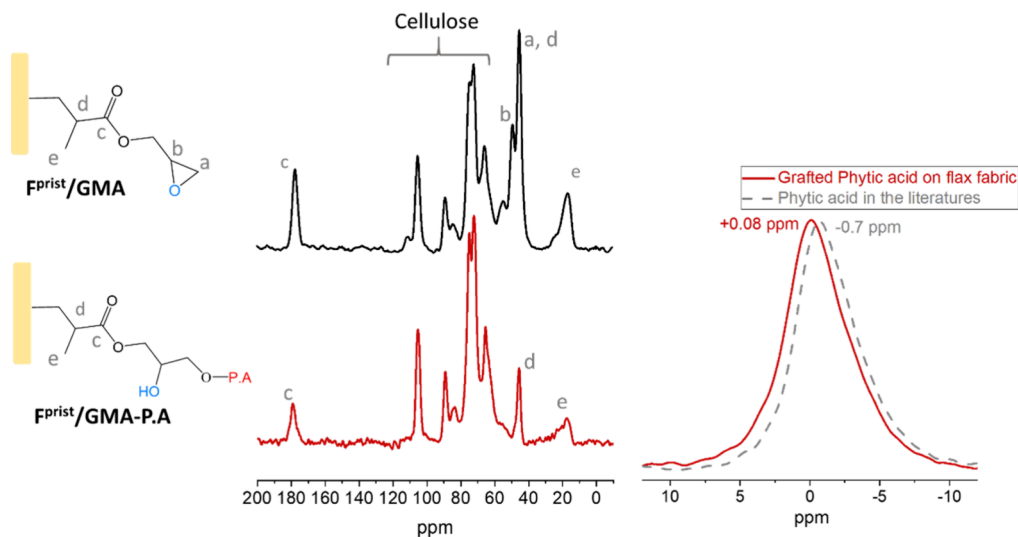


Figure 6. ^{13}C and ^{31}P NMR spectra for $\text{F}^{\text{Prist}}/\text{GMA}$ and $\text{F}^{\text{Prist}}/\text{GMA-PA}$.

hypothesis that the glycidyl groups react during the treatment process, leading to the disappearance of their particular signal.

On the other hand, the ^{31}P NMR spectrum of $\text{F}^{\text{prist}}/\text{GMA-PA}$ presents a very slight chemical shift for the signal of PA. A unique signal centered around +0.08 ppm was compared to the known PA spectrum found in the literature³⁷ (referenced to -0.7 ppm). Many researchers found a signal of phosphate ester groups bound to the cellulose near 0 ppm. For example, Antoun et al.³¹ have modified hemp fibers using PA. They found a ^{31}P main signal centered at 0 ppm related to phosphate esters bound to cellulose. Furthermore, Rol et al.³⁸ have phosphorylated cellulose fibers using different phosphate salts. They found an intense signal at 0 ppm related to the grafted phosphate ester. Also, Fiss et al.³⁹ have phosphorylated cellulose nanocrystals, and a ^{31}P main signal at +0.3 ppm was detected.

3.2.2. FTIR Spectroscopy for Modified Flax Fabrics. PA, EGDE, and the produced coating were analyzed by FTIR spectroscopy to confirm the formation of a cross-linked coating layer (Figure 7). The band corresponding to P-OH groups at

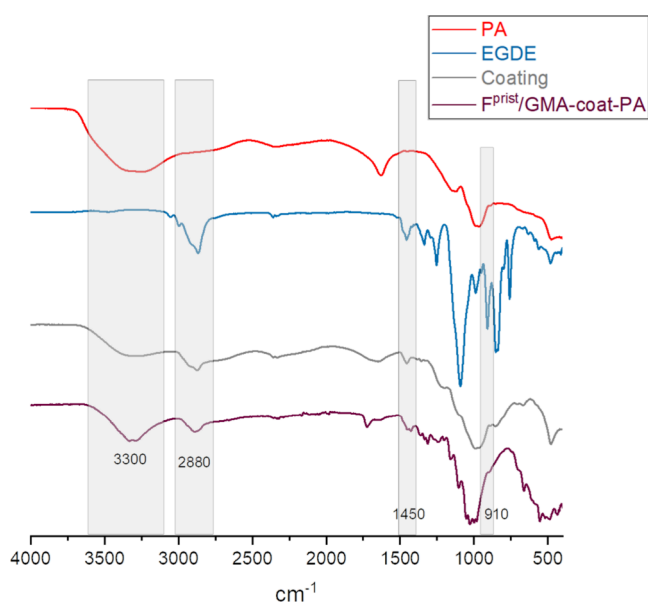


Figure 7. FTIR spectra for PA, EGDE, PA coating, and $\text{F}^{\text{prist}}/\text{GMA-coat-PA}$.

3300 cm^{-1} is observable in the PA spectra. On the other side, the band corresponding to glycidyl groups (at 907 cm^{-1}) and the bands corresponding to C-H (stretching at 2875 cm^{-1} /bending at 1450 cm^{-1}) are highlighted in the EGDE spectra. In the spectrum of the produced coating, the bands corresponding to C-H bonds are still observable while the band of glycidyl groups has disappeared. Moreover, the band corresponding to P-OH groups became less intense. This proves that the reaction occurred between the glycidyl of EGDE and the P-OH groups of PA. Also, the $\text{F}^{\text{prist}}/\text{GMA-coat-PA}$ sample was analyzed by FTIR spectroscopy and the band corresponding to C-H bending at 1450 cm^{-1} is observed without a glycidyl band appearing, confirming the successful deposition of the coating onto the fabric.

3.2.3. SEM-EDS Analysis. The distribution of chemical elements within the cross-section of flax elementary fibers was investigated through SEM-EDS analyses (Figure 8). Notably, the phosphorus mapping of the two samples $\text{F}^{\text{prist}}/\text{GMA-PA}$

and $\text{F}^{\text{Alk}}/\text{GMA-PA}$ with P content of 0.75 wt %, was done. In both cases, phosphorus element exhibited a homogeneous dispersion, extending not only across the surface but also deeply into the bulk of the fibers.

On the other hand, for $\text{F}^{\text{prist}}/\text{GMA-coat-PA}$ and $\text{F}^{\text{Alk}}/\text{GMA-coat-PA}$ samples, a contrasting trend is observed. The phosphorus element is mainly concentrated on the surface of the elementary fibers, with a limited presence within the fiber's bulk. However, some fibers for these coated samples present a uniform dispersion onto the surface as well as in the bulk of the fibers, especially with the $\text{F}^{\text{Alk}}/\text{GMA-coat-PA}$ sample, probably due to the lignin removal.

3.2.4. Thermal Behavior. Figure 9a and Figure 9b show the TGA curves of all prepared samples. The initial decomposition temperature at 5% weight loss (T_{in}), the temperature of the maximum degradation rate (T_{max}), the maximum degradation rate at T_{max} and the yield of char ($Y_{\text{char}\%}$) are listed in Table 2. A clear difference was observed in the T_{in} of fabrics during the various stages of the treatment process applied to the fabrics (Figure 9a). T_{in} has slightly decreased from $280\text{ }^{\circ}\text{C}$ for F^{prist} to $270\text{ }^{\circ}\text{C}$ for $\text{F}^{\text{prist}}/\text{GMA}$. This shift in T_{in} is due to the grafted GMA on the flax fabric. After PA grafting, T_{in} demonstrated a significant decrease, reaching values as low as $250\text{ }^{\circ}\text{C}$ for $\text{F}^{\text{prist}}/\text{GMA-PA}$ with 0.74 wt % of P content and $253\text{ }^{\circ}\text{C}$ for $\text{F}^{\text{prist}}/\text{GMA-coat-PA}$ with 1.24 wt % of P content, respectively. These early decompositions are attributed to the grafting of PA. Indeed, the modification of the flax by phosphorus molecules reduces its thermal stability, thus the fabric decomposes at lower temperatures.¹⁴ Other researchers found similar results when they modified natural fibers with phosphorus molecules. For example, Taibi et al.¹⁸ have grafted MAPC1 onto flax fabric and found a decrease in the T_{in} of the treated fabric compared to the pristine one. Also, Yasin et al.⁴⁰ have treated a cotton fabric by *N*-methylol dimethyl phosphonopropionamide and they found similar results for T_{in} .

On the other hand, the maximum degradation rate (at T_{max}) for pristine flax was $0.34\text{ wt \%}/\text{s}$. Following the grafting of GMA, this value exhibited a notable reduction, decreasing to $0.24\text{ wt \%}/\text{s}$. Subsequently, for $\text{F}^{\text{prist}}/\text{GMA-PA}$, which contained 0.74% phosphorus, the degradation rate remained relatively constant, with approximately the same value. However, a significant decrease in the degradation rate up to $0.18\text{ wt \%}/\text{s}$ was observed for $\text{F}^{\text{prist}}/\text{GMA-coat-PA}$, which contained a higher P content, about 1.24%. These results highlight the clear influence of phosphorus content on the thermal behavior of the fabrics. Furthermore, Y_{char} exhibited great variations throughout the treatment steps. Initially, for pristine flax, Y_{char} was measured at 10.9%. After GMA grafting, Y_{char} has decreased up to 1%, which indicates that GMA polymer chains inhibit the char formation of fabrics. Further investigations are needed to understand this phenomenon. However, following the subsequent grafting of PA, Y_{char} underwent a remarkable increase, reaching nearly 17% for both $\text{F}^{\text{prist}}/\text{GMA-PA}$ and $\text{F}^{\text{prist}}/\text{GMA-coat-PA}$ (Figure S3). These results display the impact of the treatment steps on the char yield, particularly highlighting the char promotion effect due to the introduction of PA. Nevertheless, it is noteworthy that the char is not stable enough until $900\text{ }^{\circ}\text{C}$ and continues to degrade over a large range of temperatures.

An identical behavior was observed across all treatment stages for the pretreated fabrics (Figure 9b). Even the values of T_{in} , the degradation rate at T_{max} and Y_{char} for $\text{F}^{\text{Alk}}/\text{GMA}$, $\text{F}^{\text{Alk}}/\text{GMA-PA}$, and $\text{F}^{\text{Alk}}/\text{GMA-coat-PA}$ are almost the same as for

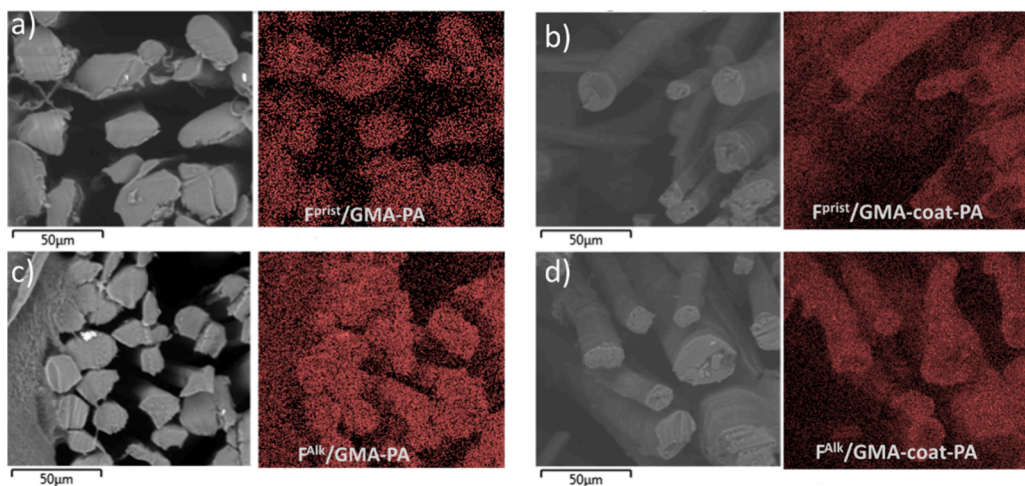


Figure 8. SEM images of (a) $F^{\text{prist}}/\text{GMA-PA}$, (b) $F^{\text{prist}}/\text{GMA-coat-PA}$, (c) $F^{\text{Alk}}/\text{GMA-PA}$, and (d) $F^{\text{Alk}}/\text{GMA-coat-PA}$, with their corresponding EDS phosphorus mappings.

pristine flax. However, pristine and delignified flax have a clear difference in terms of T_{in} and degradation rate at T_{max} . This difference can be attributed to lignin removal from the flax fibers. Previous studies have mentioned that alkali treatment of flax fibers leads to a slight improvement in thermal stability,⁴¹ resulting in a delay in thermal decomposition. Also, the treatment for the removal of lignin, which also degrades the cellulose and hemicellulose products of the fibers,⁴² significantly affects the degradation rate of the fabric.

3.2.5. Fire Behavior. The assessment of the fire behavior of the prepared samples at the microscale was performed using a PCFC test. The heat release rate (HRR) curves are shown in Figure 9c and Figure 9d, and the main data are listed in Table 3.

For pristine flax, pHRR was observed at approximately 380 °C, with a value of approximately 188 W/g. The THR value for this sample was approximately 9.5 kJ/g, which exhibited a residue content of 15.7 wt %, close to the value measured by TGA at the same temperature (i.e., 750 °C) (Figure 9c). These results indicate that the flame-retardant properties of the pristine sample were relatively good compared to the delignified flax fabric. This sample shows a pHRR of about 241 W/g, THR of 10.9 kJ/g, and a residue of 11.3 wt % (also close to the value measured by TGA) (Figure 9d). These results suggest that the presence of lignin in the flax fabric contributes to its improved flame retardancy properties compared to the delignified one. Another possibility to explain these results is that the alkaline treatment enhances the degradation of cellulose, leading to worse fire properties.

After grafting with GMA, both $F^{\text{prist}}/\text{GMA}$ and $F^{\text{Alk}}/\text{GMA}$ showed similar pHRR values, approaching 190 W/g. However, they exhibited a significantly higher THR and HCC of about 15 kJ/g and much lower residue values, approximately 3.3 and 4.8 wt %, respectively. It is noteworthy that the grafting of GMA has a detrimental effect on the flame behavior properties of these samples. Indeed, the heat of combustion of GMA calculated using Huggett's relation is 23.6 kJ/g, i.e., much higher than for flax. Then, a high grafting yield of GMA contributes to the increase in HRR. Nevertheless, this grafting step was essential for the subsequent grafting of PA.

When PA was grafted onto $F^{\text{prist}}/\text{GMA}$, the pHRR decreased to 114 W/g with a slight shift at 330 °C, and an additional pHRR (pHRR-2) appeared at around 99 W/g at 398 °C. PA

acts (i.e., it promotes charring) differently on the various components (cellulose, hemicellulose, and lignin) of the fibers. Therefore, the decomposition pathway is altered and becomes more complex with the occurrence of additional peaks. However, the THR value remained relatively high, at 12.2 kJ/g, and the residue amount was lower than that of pristine flax, standing at 11.3 wt %. This implies that $F^{\text{prist}}/\text{GMA-PA}$, which contains only 0.74 wt % of P, did not fully compensate for the detrimental effect of GMA. In contrast, its delignified counterpart, $F^{\text{Alk}}/\text{GMA-PA}$, which also contains the same amount of P, exhibited better flame retardancy characteristics. Values of pHRR are about 85 and 50 W/g, respectively, THR is about 7.3 kJ/g, and a notably high residue is observed (19.7 wt %). This suggests that the absence of lignin in $F^{\text{Alk}}/\text{GMA-PA}$ contributed to enhance flame retardancy properties compared to $F^{\text{prist}}/\text{GMA-PA}$. This effect was not expected while lignin has a better fire behavior than cellulose. This result may be due to the low efficiency of phosphorus compounds on the lignin decomposition. Indeed, the lignin does not respond effectively to the phosphorylation. Prieur et al.⁴³ have phosphorylated lignin samples using phosphorus pentoxide (P_2O_5), but after reaching 3 wt % of P content, the THR of lignin decreased only from 14.2 to 12.1 kJ/g.

On the other hand, $F^{\text{prist}}/\text{GMA-coat-PA}$ and its delignified counterpart, $F^{\text{Alk}}/\text{GMA-coat-PA}$, both exhibited better flame retardancy with a P content close to 1.3 wt %. They displayed a first pHRR around 55 W/g at 300 °C, a second pHRR around 46 and 33 w/g at 370 and 360 °C, respectively, and residues of approximately 23% and 22%, respectively (once again these residue yields are close to those measured in TGA). Nevertheless, $F^{\text{Alk}}/\text{GMA-coat-PA}$ had a lower THR compared to $F^{\text{prist}}/\text{GMA-coat-PA}$, confirming the previous result, which may be explained by the weaker response of the lignin to the phosphorylation.

Phosphorus FRs, especially phosphate and phosphonate-based FRs, are well-known to act as char promoters. At relatively low temperature, the phosphorus flame retardant decomposes and forms phosphonic acid, which leads to the formation of a phosphorus ester through the phosphorylation of the primary hydroxyl group of cellulose. Then these esters catalyze the dehydration of cellulose to enhance charring.⁴⁴ A large amount of carbon is trapped in the char. It results in a decrease of heat release and sometimes in the formation of an

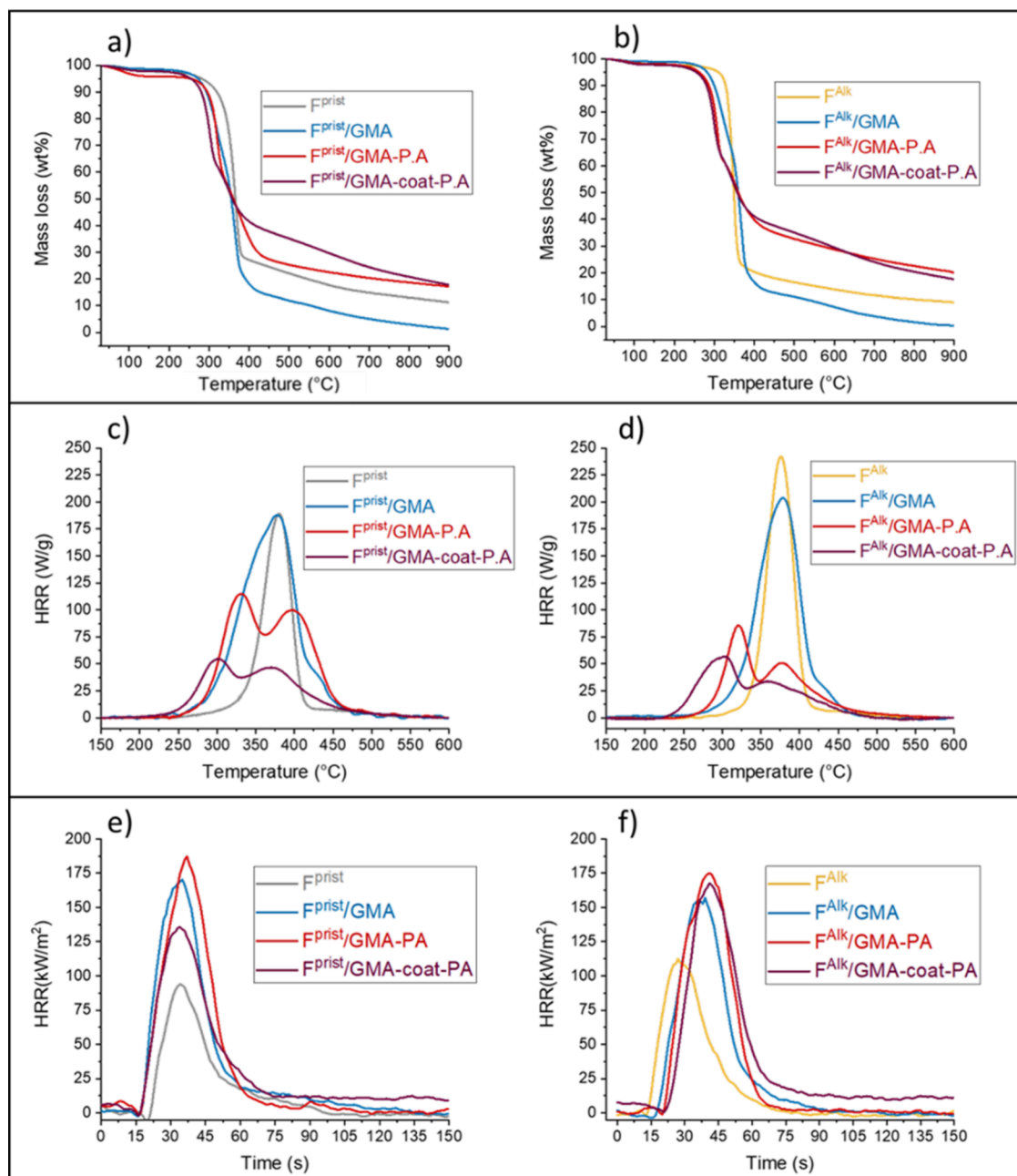


Figure 9. (a and b) TGA curves. (c and d) HRR curves obtained by PCFC analyses. (e and f) Cone calorimeter curves of pristine and delignified flax samples, respectively.

Table 2. TGA Results of the Modified Flax Samples

samples	P content (wt %)	T_{in} (°C)	T_{max} (°C)	degradation rate at T_{max} (wt %/s)	Y_{char} (%) at 900 °C
F^{prist}	-	280	365	0.34	10.9
F^{prist}/GMA	-	270	363	0.24	1
$F^{prist}/GMA-PA$	0.74	252	320	0.22	16.9
$F^{prist}/GMA-coat-PA$	1.24	253	302	0.18	17.4
F^{Alk}	-	308	348	0.53	8.8
F^{Alk}/GMA	-	279	366	0.3	0.3
$F^{Alk}/GMA-PA$	0.79	253	309	0.23	19.3
$F^{Alk}/GMA-coat-PA$	1.3	254	298	0.19	17.2

insulating char barrier layer. Nevertheless, in the case of thin samples such as fabrics, the barrier effect is not effective. These

results align with the findings of other researchers concerning pHRR values, as demonstrated by Taibi et al.¹⁸ and Hajj et al.,¹⁹ who treated flax fabrics with different phosphorus monomers (Figure S4). However, there is a slight deviation in terms of THR values, which may be attributed to the presence of GMA grafting onto fabrics, which greatly increases the HRR.

The fire behavior of the prepared samples was also performed at the bench scale using a cone calorimeter test at 35 kW/m² (Figure 9e, Figure 9f, and Table 4).

For pristine and delignified flax samples, pHRR is close to 100 kW/m² and THR is about 13.5 and 15.9 kJ/g, respectively. As mentioned above, this difference is supposed to be due to lignin removal. These THR values are both higher than those measured by PCFC due to the thermo-oxidation of char at the

Table 3. Main Data from the PCFC Test

samples	P content (wt %)	pHRR (W/g)	temperature of pHRR (°C)	pHRR-2 (W/g)	temperature of pHRR-2 (°C)	THR (kJ/g)	HCC (kJ/g)	residue (wt %)
F ^{prist}	-	188	380	-	-	9.5	11.3	15.7
F ^{prist} /GMA	-	186	376	-	-	14.9	15.4	3.3
F ^{prist} /GMA-PA	0.74	114	330	99	398	12.2	13.8	11.3
F ^{prist} /GMA-coat-PA	1.24	54	301	46	370	7	9.1	23
F ^{Alk}	-	241	377	-	-	10.9	12.0	9.3
F ^{Alk} /GMA	-	203	378	-	-	15.1	15.9	4.8
F ^{Alk} /GMA-PA	0.79	85	320	50	377	7.3	9.1	19.7
F ^{Alk} /GMA-coat-PA	1.3	56	302	33	360	4.9	6.3	22

Table 4. Main Data from the Cone Calorimeter Test

samples	P content (wt %)	initial mass (g)	TTI (s)	pHRR (kW/m ²)	THR (MJ/m ²)	THR (kJ/g)	EHC (kJ/g)	residue (%)
F ^{prist}	-	1.5	19	94	2.29	13.5	13.5	0.0
F ^{prist} /GMA	-	2.4	16	170	4.58	16.9	16.9	0.0
F ^{prist} /GMA-PA	0.74	2.8	16	187	4.67	14.7	15.7	6.2
F ^{prist} /GMA-coat-PA	1.24	3.5	16	135	5.2	8.1	9.5	14.8
F ^{Alk}	-	1.5	13	112	2.7	15.9	15.9	0.0
F ^{Alk} /GMA	-	2.1	16	156	4.12	17.3	17.3	0.0
F ^{Alk} /GMA-PA	0.79	2.8	20	174	4.51	14.2	15.4	7.3
F ^{Alk} /GMA-coat-PA	1.3	3.9	21	167	6.44	9.2	10.7	14.4

end of the cone test. Indeed, the residue yield is null for both samples. For the same reason, EHC values are higher than HCC in PCFC. TTI is reduced for the delignified sample (13 versus 19 s).

After grafting with GMA, both F^{prist}/GMA and F^{Alk}/GMA exhibit a significantly higher pHRR (170 and 156 kW/m², respectively) and THR (16.9 and 17.3 kJ/g, respectively). Residues are still negligible. TTI are similar (16 s).

After grafting with PA, F^{prist}/GMA-PA and its delignified counterpart F^{Alk}/GMA-PA with 0.7% of P content demonstrate a decrease of THR to 14.7 and 14.2 kJ/g, respectively, while residue yield increases to 6.2 and 7.3 wt %, respectively. These residue yields remain significantly lower compared to those measured in PCFC, evidencing the thermo-oxidation of char after flame out, when pyrolysis becomes aerobic. TTI does not change significantly (16–20 s). Unexpectedly, pHRR is not reduced and even tends to slightly increase (around 180 kW/m²) despite the presence of phosphorus. This unexpected trend is explained below.

For F^{prist}/GMA-coat-PA and F^{Alk}/GMA-coat-PA with a higher content of P (about 1.3%), all fire properties are more favorable: pHRR decreases to 135 and 167 kW/m², THR decreases to 8.1 and 9.2 kJ/g, EHC decreases to 9.5 and 10.7 kJ/g, and residue yield increases to 14.8 and 14.4 wt %, respectively. The increase in residue yield highlights the role of PA as a char promoter (Figure S5 and Figure S6). Nevertheless, note once again that residue yields are still lower than the corresponding values in PCFC, due to the thermo-oxidation of char.

It is also noteworthy that the coating process allows the reduction of THR in comparison to pristine and delignified fabrics but not the pHRR, which remains higher (but slightly lower than pHRR for F^{prist}/GMA and F^{Alk}/GMA). In a previous work,⁴⁵ we have shown that the pHRR of thin materials as fabrics depends only on the heat flux, the effective heat of combustion, and the fabric mass. For such thin materials, the higher the mass, the higher the amount of fuels released a few seconds after ignition contributing to pHRR, and thus the higher the pHRR. However, the flax

modification significantly increases the area density and then the initial mass of the samples (see Table 4). Moreover, GMA grafting leads to an increase of EHC. Higher initial mass and EHC both explain probably why the pHRR of phosphorus-containing samples remains high despite a significant phosphorus content. For coated samples, the increase of mass is even higher. Nevertheless, the phosphorus content is also higher leading to a significant charring and a decrease of EHC. Therefore, pHRR does not increase anymore and even tends to decrease, but it does not reach the lower values observed for pristine and delignified flax samples.

While PA is a good candidate as a bioresource flame retardant, it is important to consider that the use of acidic solutions, such as PA, directly on the fibers has a negative impact on the mechanical properties. Indeed, the acidic solution can induce a degradation of the cellulose chains and its molecular weight decrease, thus reducing their strength. This is considered as a notable drawback of these treatments.^{46–48}

CONCLUSION

Flax fabrics have been successfully grafted with GMA through a simultaneous e-beam irradiation procedure. By taking advantage of the reaction between glycidyl and P–OH groups, a postgrafting of PA was subsequently performed on the fabrics, producing a flax fabric with a P content of 0.74 wt %.

Another method was applied to introduce PA and increased the P content up to 1.24 wt % via a dip-coating process using EGDE as the cross-linking agent. The double glycidyl functions of this molecule engaged in reactions with PA, creating a cross-linked coating on the fiber surface, which in turn increases the P content.

An alkaline pretreatment (in order to remove lignin) was found to be highly favorable to increase the grafting yield of GMA. This process resulted in a remarkable increase, about 50%, in mass gain compared to the pristine samples under identical conditions.

In order to assess the influence of lignin on flame retardancy, grafting of PA was performed on pristine and delignified fabrics, adjusting treatment conditions to yield nearly an equivalent P content, approximately 0.79% and 1.3% for direct grafting and dip-coating techniques, respectively.

TGA results demonstrated an increase of the maximum degradation rate coupled with a reduction in char residue after GMA grafting. Conversely, after introducing PA, a contrasting effect was observed: the maximum degradation rate decreased, while the char residue increased, for both pristine and delignified fabrics. Furthermore, PCFC results illustrated an increase in THR and a decrease in the residue for both pristine and delignified fabrics after GMA grafting. When PA was introduced, a decrease of THR and an increase of the residue occurred for both types of fabrics. Nevertheless, the effect of P (for a limited P content of 0.7 wt %) appears to be more significant for delignified fabrics. However, no difference was recognized between them at a P content of 1.3%. Cone calorimetry confirmed some results obtained in PCFC, namely the char promotion and the reduction of THR in the presence of PA, especially for the dip-coating process (providing the highest content of P). Nevertheless, pHRR was not reduced and even increased in comparison to pristine and pretreated fabrics. These results may be explained by the increase of EHC (due to GMA grafting) and area density of fabrics after modification.

In this study, PA was covalently grafted onto the surface of flax fibers, which gives a potential durability of the flame-retardant properties. Nevertheless, the durability of these treatments will be extensively investigated in future studies in order to verify their effectiveness.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.4c00198>.

Preparation technique of the flax fabric sample, the linear relationship between P content of modified fabrics and the grafting rate of GMA, the degradation rate as a function of P content for all prepared samples, a comparison between our results and the other researchers' results in terms of THR and pHRR, photos for the residue after the cone calorimetry analysis, and the data of the P content for all prepared samples (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Rodolphe Sonnier – PCH, IMT – Mines Alès, 30100 Alès, France; orcid.org/0000-0001-6487-7299;
Email: rodolphe.sonnier@mines-ales.fr

Authors

Antoine Ishak – PCH, IMT – Mines Alès, 30100 Alès, France
Claire Longuet – PCH, IMT – Mines Alès, 30100 Alès, France
Belkacem Otazaghine – PCH, IMT – Mines Alès, 30100 Alès, France; orcid.org/0000-0003-1967-9984

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsapm.4c00198>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge our colleagues in (C2MA, PCH, IMT Mines Alès) Jean-Claude ROUX for SEM-EDS images, Romain Ravel for the training on the ICP-AES analysis, Loïc Dumazert for the training of PCFC and cone calorimetry analysis, and IMT Mines Alès for financing this work.

■ REFERENCES

- (1) Bunsell, A. R. *Introduction to the Science of Fibers*; Elsevier Ltd., 2018. DOI: [10.1016/B978-0-08-101272-7.00001-8](https://doi.org/10.1016/B978-0-08-101272-7.00001-8).
- (2) Mngomezulu, M. E.; John, M. J.; Jacobs, V.; Luyt, A. S. Review on Flammability of Biofibres and Biocomposites. *Carbohydr. Polym.* **2014**, *111*, 149–182.
- (3) Chai, M. W.; Bickerton, S.; Bhattacharyya, D.; Das, R. Influence of Natural Fibre Reinforcements on the Flammability of Bio-Derived Composite Materials. *Compos. Part B Eng.* **2012**, *43* (7), 2867–2874.
- (4) Mayer-Gall, T.; Knittel, D.; Gutmann, J. S.; Opwis, K. Permanent Flame Retardant Finishing of Textiles by Allyl-Functionalized Polyphosphazenes. *ACS Appl. Mater. Interfaces* **2015**, *7* (18), 9349–9363.
- (5) Cheng, W.; Zhang, Y.; Tian, W.; Liu, J.; Lu, J.; Wang, B.; Xing, W.; Hu, Y. Highly Efficient MXene-Coated Flame Retardant Cotton Fabric for Electromagnetic Interference Shielding. *Ind. Eng. Chem. Res.* **2020**, *59* (31), 14025–14036.
- (6) Li, P.; Wang, B.; Xu, Y. J.; Jiang, Z.; Dong, C.; Liu, Y.; Zhu, P. Erratum: Ecofriendly Flame-Retardant Cotton Fabrics: Preparation, Flame Retardancy, Thermal Degradation Properties, and Mechanism (ACS Sustainable Chem. Eng. (2019) 7:23 (19246–19256)) DOI: [10.1021/acsuschemeng.9b05523](https://doi.org/10.1021/acsuschemeng.9b05523). *ACS Sustain. Chem. Eng.* **2021**, *9* (6), 2616–2618.
- (7) Zope, I. S.; Foo, S.; Seah, D. G. J.; Akunuri, A. T.; Dasari, A. Development and Evaluation of a Water-Based Flame Retardant Spray Coating for Cotton Fabrics. *ACS Appl. Mater. Interfaces* **2017**, *9* (46), 40782–40791.
- (8) Miao, Z.; Yan, D.; Zhang, T.; Yang, F.; Zhang, S.; Liu, W.; Wu, Z. High-Efficiency Flame Retardants of a P-N-Rich Polyphosphazene Elastomer Nanocoating on Cotton Fabric. *ACS Appl. Mater. Interfaces* **2021**, *13* (27), 32094–32105.
- (9) Opwis, K.; Wego, A.; Bahners, T.; Schollmeyer, E. Permanent Flame Retardant Finishing of Textile Materials by a Photochemical Immobilization of Vinyl Phosphonic Acid. *Polym. Degrad. Stab.* **2011**, *96* (3), 393–395.
- (10) Parvinzadeh Gashti, M.; Almasian, A. UV Radiation Induced Flame Retardant Cellulose Fiber by Using Polyvinylphosphonic Acid/Carbon Nanotube Composite Coating. *Compos. Part B Eng.* **2013**, *45* (1), 282–289.
- (11) Tsafack, M. J.; Levalois-Grützmacher, J. Flame Retardancy of Cotton Textiles by Plasma-Induced Graft-Polymerization (PIGP). *Surf. Coat. Technol.* **2006**, *201* (6), 2599–2610.
- (12) Alongi, J.; Ciobanu, M.; Malucelli, G. Sol-Gel Treatments for Enhancing Flame Retardancy and Thermal Stability of Cotton Fabrics: Optimisation of the Process and Evaluation of the Durability. *Cellulose* **2011**, *18* (1), 167–177.
- (13) Sonnier, R.; Otazaghine, B.; Viretto, A.; Apolinario, G.; Lenny, P. Improving the Flame Retardancy of Flax Fabrics by Radiation Grafting of Phosphorus Compounds. *Eur. Polym. J.* **2015**, *68*, 313–325.
- (14) Hajj, R.; Otazaghine, B.; Sonnier, R.; El Hage, R.; Rouif, S.; Nakhil, M.; Lopez-Cuesta, J. M. Influence of Monomer Reactivity on Radiation Grafting of Phosphorus Flame Retardants on Flax Fabrics. *Polym. Degrad. Stab.* **2019**, *166*, 86–98.
- (15) Teixeira, M.; Sonnier, R.; Otazaghine, B.; Ferry, L.; Aubert, M.; Tirri, T.; Wilén, C. E.; Rouif, S. Radiation-Grafting of Flame Retardants on Flax Fabrics - A Comparison between Different Flame Retardant Structures. *Radiat. Phys. Chem.* **2018**, *145*, 135–142.
- (16) Abou Elmaaty, T.; Okubayashi, S.; Elsis, H.; Abouelenin, S. Electron Beam Irradiation Treatment of Textiles Materials: A Review. *J. Polym. Res.* **2022**, *29* (4), n/a.

- (17) Khan, F. Characterization of Methyl Methacrylate Grafting onto Preirradiated Biodegradable Lignocellulose Fiber by γ -Radiation. *Macromol. Biosci.* **2005**, *5* (1), 78–89.
- (18) Taibi, J.; Rouif, S.; Clément, J. L.; Ameduri, B.; Sonnier, R.; Otazaghine, B. Flame Retardancy of Flax Fibers by Pre-Irradiation Grafting of a Phosphonate Monomer. *Ind. Crops Prod.* **2022**, *176*, 114334.
- (19) Hajj, R.; El Hage, R.; Sonnier, R.; Otazaghine, B.; Gallard, B.; Rouif, S.; Nakhil, M.; Lopez-Cuesta, J. M. Grafting of Phosphorus Flame Retardants on Flax Fabrics: Comparison between Two Routes. *Polym. Degrad. Stab.* **2018**, *147*, 25–34.
- (20) Malucelli, G.; Bosco, F.; Alongi, J.; Carosio, F.; Di Blasio, A.; Mollea, C.; Cuttica, F.; Casale, A. Biomacromolecules as Novel Green Flame Retardant Systems for Textiles: An Overview. *RSC Adv.* **2014**, *4* (86), 46024–46039.
- (21) Barbalini, M.; Bartoli, M.; Tagliaferro, A.; Malucelli, G. Phytic Acid and Biochar: An Effective All Bio-Sourced Flame Retardant Formulation for Cotton Fabrics. *Polymers (Basel)*. **2020**, *12* (4), 811.
- (22) Zilke, O.; Plohl, D.; Opwis, K.; Mayer-Gall, T.; Gutmann, J. S. A Flame-Retardant Phytic-Acid-Based LbL-Coating for Cotton Using Polyvinylamine. *Polymers (Basel)*. **2020**, *12* (5), 1202.
- (23) Sykam, K.; Forsth, M.; Sas, G.; Restas, A.; Das, O. Phytic Acid: A Bio-Based Flame Retardant for Cotton and Wool Fabrics. *Ind. Crops Prod.* **2021**, *164* (June), 113349.
- (24) Liu, Y.; Zhang, A.; Cheng, Y.; Li, M.; Cui, Y.; Li, Z. Recent Advances in Biomass Phytic Acid Flame Retardants. *Polym. Test.* **2023**, *124* (May), 108100.
- (25) Ehsanimehr, S.; Sonnier, R.; Badawi, M.; Ducos, F.; Kadi, N.; Skrifvars, M.; Saeb, M. R.; Vahabi, H. Sustainable Flame-Retardant Flax Fabrics by Engineered Layer-by-Layer Surface Functionalization with Phytic Acid and Polyethylenimine. *Fire Technol.* **2023**, *19*, n/a.
- (26) Cheng, X. W.; Guan, J. P.; Chen, G.; Yang, X. H.; Tang, R. C. Adsorption and Flame Retardant Properties of Bio-Based Phytic Acid on Wool Fabric. *Polymers (Basel)*. **2016**, *8* (4), 122.
- (27) Kang, M.; Chen, S.; Yang, R.; Li, D.; Zhang, W. Fabrication of an Eco-Friendly Clay-Based Coating for Enhancing Flame Retardant and Mechanical Properties of Cotton Fabrics via LbL Assembly. *Polymers (Basel)*. **2022**, *14* (22), 4994.
- (28) Malucelli, G. Layer-by-Layer Assembly: A Novel Flame-Retardant Solution to Polymeric Materials. *Flame Retard. Polym. Mater. A Handb.* **2019**, 119–133.
- (29) Feng, Y.; Zhou, Y.; Li, D.; He, S.; Zhang, F.; Zhang, G. A Plant-Based Reactive Ammonium Phytate for Use as a Flame-Retardant for Cotton Fabric. *Carbohydr. Polym.* **2017**, *175*, 636–644.
- (30) Liu, X.-h.; Zhang, Q.-y.; Cheng, B.-w.; Ren, Y.-l.; Zhang, Y.-g.; Ding, C. Durable Flame Retardant Cellulosic Fibers Modified with Novel, Facile and Efficient Phytic Acid-Based Finishing Agent. *Cellulose* **2018**, *25* (1), 799–811.
- (31) Antoun, K.; Ayadi, M.; El Hage, R.; Nakhil, M.; Sonnier, R.; Gardiennet, C.; Le Moigne, N.; Besserer, A.; Brosse, N. Renewable Phosphorous-Based Flame Retardant for Lignocellulosic Fibers. *Ind. Crops Prod.* **2022**, *186* (March), 115265.
- (32) Desmet, G.; Takács, E.; Wojnárovits, L.; Borsa, J. Cellulose Functionalization via High-Energy Irradiation-Initiated Grafting of Glycidyl Methacrylate and Cyclodextrin Immobilization. *Radiat. Phys. Chem.* **2011**, *80* (12), 1358–1362.
- (33) Aslan, A.; Çelik, S. Ü.; Bozkurt, A. Proton-Conducting Properties of the Membranes Based on Poly(Vinyl Phosphonic Acid) Grafted Poly(Glycidyl Methacrylate). *Solid State Ionics* **2009**, *180* (23–25), 1240–1245.
- (34) Ma, G.; Wang, X.; Cai, W.; Ma, C.; Wang, X.; Zhu, Y.; Kan, Y.; Xing, W.; Hu, Y. Preparation and Study on Nitrogen- and Phosphorus-Containing Fire Resistant Coatings for Wood by UV-Cured Methods. *Front. Mater.* **2022**, *9* (March), 1–10.
- (35) Iqra, A. R.; Ayesha, A.; Muhammad, F. S.; Asra, T. Multi-Functional Carbon Fiber Reinforced Composites for Fire Retardant Applications. *Key Eng. Mater.* **2021**, *875*, 23–28.
- (36) Le Moigne, N.; Sonnier, R.; El Hage, R.; Rouif, S. Radiation-Induced Modifications in Natural Fibres and Their Biocomposites: Opportunities for Controlled Physico-Chemical Modification Pathways? *Ind. Crops Prod.* **2017**, *109*, 199–213.
- (37) Barbalini, M.; Bertolla, L.; Toušek, J.; Malucelli, G. Hybrid Silica-Phytic Acid Coatings: Effect on the Thermal Stability and Flame Retardancy of Cotton. *Polymers (Basel)*. **2019**, *11* (10), 1664.
- (38) Rol, F.; Sillard, C.; Bardet, M.; Yarava, J. R.; Emsley, L.; Gablin, C.; Léonard, D.; Belgacem, N.; Bras, J. Cellulose Phosphorylation Comparison and Analysis of Phosphate Position on Cellulose Fibers. *Carbohydr. Polym.* **2020**, *229*, 115294.
- (39) Fiss, B. G.; Hatherly, L.; Stein, R. S.; Friščić, T.; Moores, A. Mechanochemical Phosphorylation of Polymers and Synthesis of Flame-Retardant Cellulose Nanocrystals. *ACS Sustain. Chem. Eng.* **2019**, *7* (8), 7951–7959.
- (40) Yasin, S.; Curti, M.; Rovero, G.; Behary, N.; Perwuelz, A.; Giraud, S.; Migliavacca, G.; Chen, G.; Guan, J. Flame Retardant End of Life. *BioResources* **2017**, *12* (3), S196–S211.
- (41) Gassan, J.; Bledzki, A. K. Thermal Degradation of Flax and Jute Fibers. *J. Appl. Polym. Sci.* **2001**, *82* (6), 1417–1422.
- (42) Brebu, M.; Vasile, C. Thermal Degradation of Lignin - A Review. *Cellul. Chem. Technol.* **2010**, *44* (9), 353–363.
- (43) Prieur, B.; Meub, M.; Wittemann, M.; Klein, R.; Bellayer, S.; Fontaine, G.; Bourbigot, S. Phosphorylation of Lignin: Characterization and Investigation of the Thermal Decomposition. *RSC Adv.* **2017**, *7* (27), 16866–16877.
- (44) Chapple, S.; Anandjiwala, R. Flammability of Natural Fiber-Reinforced Composites and Strategies for Fire Retardancy: A Review. *J. Thermoplast. Compos. Mater.* **2010**, *23* (6), 871–893.
- (45) El Gazi, M.; Sonnier, R.; Giraud, S.; Batistella, M.; Basak, S.; Dumazert, L.; Hajj, R.; El Hage, R. Fire Behavior of Thermally Thin Materials in Cone Calorimeter. *Polymers (Basel)*. **2021**, *13* (8), 1297.
- (46) Yu, S.; Xia, Z.; Kiratitanavit, W.; Kulkarni, S.; Kumar, J.; Mosurkal, R.; Nagarajan, R. Facile Microwave Assisted Flame Retardant Treatment for Cotton Fabric Using a Biobased Industrial Byproduct: Phytic Acid. *Cellulose* **2021**, *28* (16), 10655–10674.
- (47) Sykam, K.; Forsth, M.; Sas, G.; Restas, A.; Das, O. Phytic Acid: A Bio-Based Flame Retardant for Cotton and Wool Fabrics. *Ind. Crops Prod.* **2021**, *164*, 113349.
- (48) Wang, J.; Liu, J. *Surface Modification of Textiles by Aqueous Solutions*; Woodhead Publishing Limited, 2009. DOI: [10.1533/978184569689.269](https://doi.org/10.1533/978184569689.269).