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Flame retardancy of flax fibers by pre-irradiation grafting of phosphorus monomer

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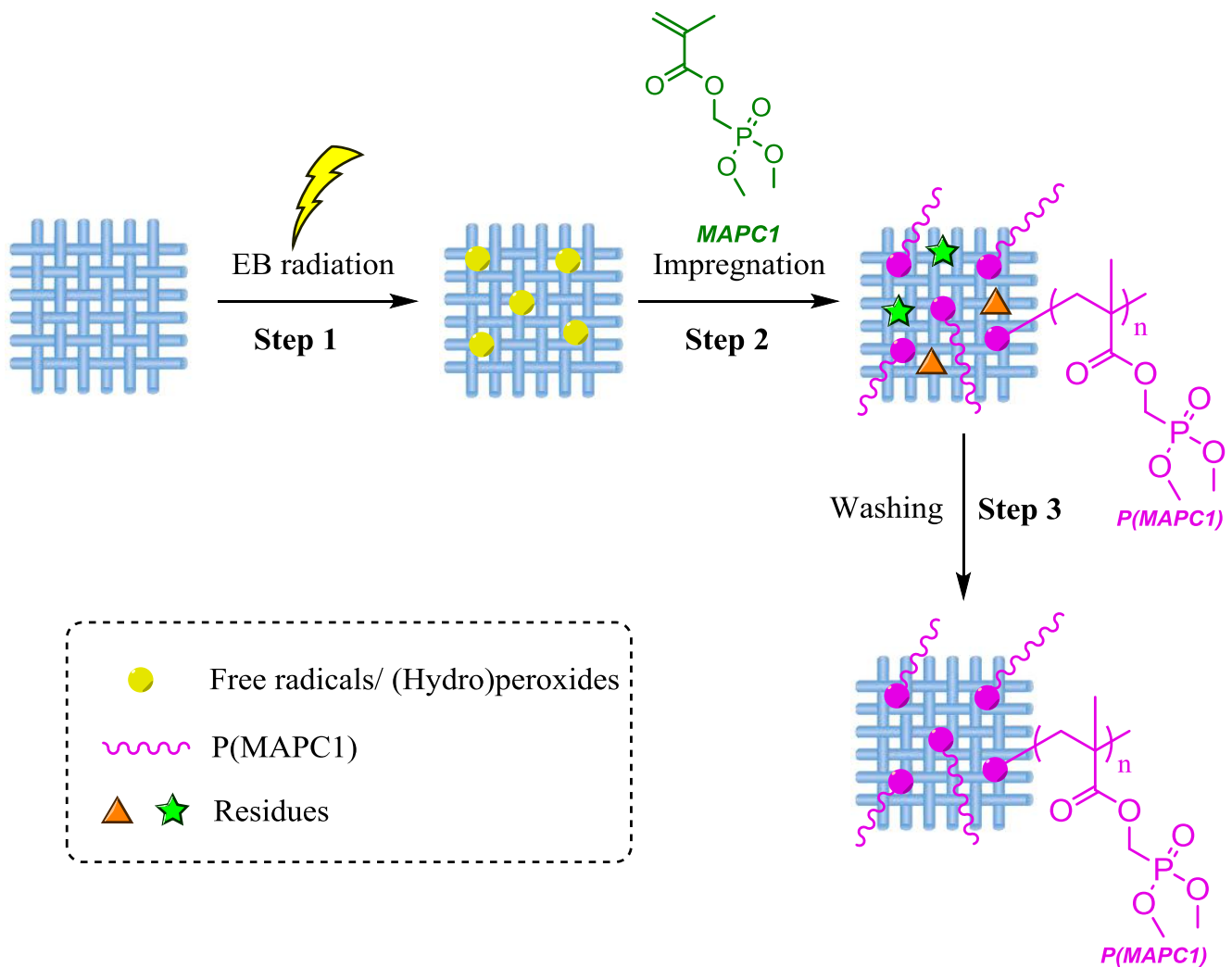
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Abstract

This study reports the functionalization of natural fibers aiming to improve their flame retardancy. Flax fabrics were modified by pre-irradiation grafting method using electron beam radiation treatment. A phosphorus-based flame retardant (FR) dimethyl(methacryloxy)methyl phosphonate (MAPC1), was used as flame retardant grafting agent. The grafting process follows three main steps. Flax fibers were first irradiated at a dose ranging between 5 and 100 kGy and stored cold to preserve the radicals created over the long period before being immersed into an aqueous solution containing MAPC1 monomer. Finally, a washing step of the treated fibers allowed to remove the unreacted monomer units but also the free oligomers and polymers chains which were not covalently bonded to the flax structure. The presence of free radicals on the flax fibers after irradiation was confirmed by Electron Paramagnetic Resonance (EPR). Grafting efficiency was evidenced by infrared spectroscopy (FTIR) and quantified using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The location of the grafted phosphorus polymer chains in the fibers structure was assessed by Scanning Electron Microscope coupled with Energy Dispersive X-ray spectrometer (SEM-EDX). The effect of phosphorus grafting on the thermal properties and fire behavior of flax fibers was studied using thermogravimetric analysis (TGA), pyrolysis combustion flow calorimetry (PCFC) and a preliminary fire test. Different parameters were monitored such as radiation dose, monomer concentration, temperature and reaction duration on the grafting efficiency. In particular, it has been observed that MAPC1 was grafted in a homogeneous way into the bulk of the elementary flax fibers leading to high phosphorus content of around 2 wt% for a dose of 10 kGy and up to 7 wt% for a dose of 100 kGy.

Keywords: Pre-irradiation, E-beam, Flax fibers, Flame retardancy, Grafting, Phosphonated monomer.



1. Introduction

Due to environment and sustainability issues, the textile industry has a significant revival of interest in the use and valorization of plant fibers (cotton, flax, jute, kenaf...) because of their numerous advantages such as renewability, biodegradability, good availability, low cost, low density, non-toxicity and good mechanical properties [1,2]. However, these plant fibers have also several disadvantages such as poor flammability properties [3–5]. Flax, which belongs to bast fibers, is one of the most widely used natural fibers in the textile market with a high added value [6].

As a matter of fact, most common textile materials are flammable with a rapid spread of flames, thus inducing hazardous fires with enormous loss of materials and fatal accidents. Therefore, protection of flammable materials against fire is necessary. To reach such a target, new legal requirements force the textile industry to modify the composition of some of their products so that they are flame retardant and difficult to ignite [7]. The most commonly used flame retardants (FRs) are phosphorus, halogen, nitrogen, silicon-based, and mineral products [4]. From a toxicity point of view, phosphorus-based retardants are considered a better

sustainable solution than halogenated ones. They generally promote charring, leading to a protective layer that helps preventing from flame spread.

Different methods have been described in the literature to modify natural fibers [8] and to improve their flame retardancy, such as UV irradiation [9], plasma treatment [10], sol-gel treatment [11–13], gamma or e-beam irradiation in order to create a chemical covalent bond with the FR molecules [14–17].

Radiation-induced graft polymerization has been described in the literature to modify natural fibers with polymer chains. Three ways for grafting under ionizing conditions can be used: (i) simultaneous grafting, [18–20], (ii) grafting by pre-irradiation in inert atmosphere [21–23] or (iii) in air [20,24]. Simultaneous grafting is based on irradiation of the fibers when they are in contact with molecules or polymers chosen for the grafting. On the other hand, the pre-irradiation consists in a first step of irradiation of the natural fibers followed by a second step where the molecules or polymers for the grafting are put in contact with the treated fibers. Grafting is due to the reaction between these molecules or macromolecules and the free radicals formed in the fiber structure during the irradiation step. These radicals have a limited lifetime and require rapid contact with the molecules used for the grafting or a cold storage. However, in presence of oxygen, some of the radicals formed can be converted into peroxide and hydroperoxide species. These hydro(peroxide) groups can then be reactivated in a subsequent step and make it possible to re-create active sites to induce grafting. [25]

In previous works, flame retardancy of natural fibers was successfully carried out by simultaneous radiation grafting of various phosphorus-based flame retardant monomers [15–17]. Nevertheless, simultaneous radiation grafting needs to perform impregnation of fibers by the grafting agent before irradiation while the pre-irradiation provides a more flexible industrial process. Indeed, the pre-irradiation grafting step, the impregnation of the fibers by the treatment agent, the grafting reaction and the washing step are carried out in sequence. So, the procedure is therefore simpler and requires less transfer of material which may be more convenient for some industries.

This article focusses on the pre-irradiation grafting. Several studies have been developed on the pre-irradiation process to graft polymer chains by initiating the polymerization of monomers from natural fibers structure. Khan [24] studied the grafting efficiency of methyl methacrylate (MMA) on jute fibers using an emulsion solution. In their study, the jute fibers were irradiated by gamma radiation (^{60}Co) in the presence of air or nitrogen. After irradiation, the fibers were stored at $-20\text{ }^{\circ}\text{C}$ to preserve the free radicals and peroxides groups formed. Then, the irradiated fibers were immersed into an MMA/emulsifier/water emulsion. Authors showed that fibers irradiated in air at 100 kGy displayed a maximum grafting rate of 73 wt% significantly higher than that achieved in N_2 (53 wt%) when the MMA concentration was fixed at 10 wt% and the polymerization temperature was $80\text{ }^{\circ}\text{C}$. Using the same grafting method, Sharif et al. [22] grafted glycidyl methacrylate on delignified kenaf fibers (GMA-g-Kenaf). The kenaf fibers were pretreated with a sodium chlorite solution (NaClO_2) to reduce the content of lignin which prevents grafting. Then, the treated fibers were irradiated by elec-

tron beam followed by a grafting reaction in a GMA/emulsifier/water emulsion. The authors showed that the grafting rate increased with the radiation dose, reaction time, reaction temperature and monomer concentration as well as with the decrease of the lignin content. The grafting rate for untreated kenaf fibers with 14.3 wt% of lignin content was about 29 wt% while for delignified fibers with a lignin content of 3.3 wt%, this rate was about 172 wt%. Other work by Mohamed et al. [23] concerned the grafting by a pre-irradiation procedure of 4-chloromethylstyrene (CMS) on kenaf fibers. Delignified kenaf fibers were irradiated under E-beam radiation at 150 kGy in nitrogen atmosphere at -20 °C. After irradiation, the fibers were immersed into a CMS emulsion previously deaerated with nitrogen at 30 °C. The influence of three parameters on grafting degree (Dg) was studied: micelle size, CMS concentration and reaction time. For a concentration of 5 wt% of CMS, the Dg increases very rapidly to 112 wt% for 4 hours of reaction before achieving its highest value of 133 wt% after 24 hours. In addition, it was observed that grafting efficiency was relatively higher for the largest micelles (at 350 nm and 500 nm). More precisely, the large micelles are composed of thermally unstable double and multiple emulsions. The contact of the double and multiple emulsions with the active radicals on the irradiated kenaf fibers contributes to the expulsion of these emulsions in smaller micelles cumulated on the surface of the fibers and leads to the grafting increase.

A previous work was carried out using simultaneous grafting method. Sonnier et al. [16] reported the grafting reactivity of two flame retardants, namely dimethylvinyl phosphonate (MVP) and dimethyl(methacryloxy)methyl phosphonate (MAPC1) on flax fibers using electron beam irradiation. The MVP was grafted into the bulk of the elemental fiber while the MAPC1 was only located on the surface. The phosphorus content reached 4 wt% after dipping flax fibers irradiated at 50 kGy in a 10 wt% solution of MVP in tetrahydrofuran (THF). The self-extinguishing fabrics were prepared with only 1.5 wt% of phosphorus. Teixeira et al. [17] compared the grafting of three FRs-based on phosphorus, bromine and sulfonamide using radiation grafting. The success of this method depends on a fast diffusion of the FR into the fibers, a low volatilization during the period between impregnation and irradiation and a high grafting efficiency. Grafting is negligible for the bromine FR and the sulfonamide FR, probably because these molecules are efficient radical scavengers or because the carbon-carbon double bond of these molecules is not reactive enough during irradiation. Only the phosphonated monomer was significantly grafted onto flax. Self-extinguishment was obtained for fabrics containing 0.5 wt% of phosphorus. Hajj et al. [14] compared two chemical routes and radiation grafting using vinyl phosphonic acid (VPA). Chemical modification under severe conditions (DMF at 160 °C) was much more promising with a phosphorus content of up to 2.3 wt%. However, chemical modification under less severe conditions (ethanol/water or DMF at 100 °C) was not effective. The phosphorus yields after grafting under less severe conditions were very low (< 0.25 wt%), due to the condensation of phosphonic acid on the phenol groups present in the lignin fraction. As the lignin content of flax is very low (generally about 2.7 wt%), the possibility of grafting phosphonic functions can therefore be limited. Radiation-grafting of VPA has been more successful. The phosphorus content reached 1.4 wt% for the fibers irradiated at 50 kGy and treated with 10 wt% of an aqueous VPA solution. Self-extinguishing properties were observed in this case.

Indeed, the radiation grafting method was considered to be more suitable than chemical grafting for natural fibers containing a low lignin content. In another study, Hajj et al. [15] studied the reactivity and grafting efficiency of different phosphorus monomers: (acryloyloxy)methyl phosphonic acid (hPAAPC1), (methacryloyloxy)methyl phosphonic acid (hPMAPC1), dimethyl(methacryloyloxy)methyl phosphonate (MAPC1), allyl phosphonic acid (APA), vinyl phosphonic acid (VPA) and dimethylvinyl phosphonate (MVP) under electron beam irradiation on flax fibers. Different parameters such as the radiation dose, the monomer concentration and the nature of the solvent (for impregnation and washing) were studied to determine their influence on the grafting content. It was observed that the increase of the absorbed dose and the monomer concentration in impregnation solution results in a higher phosphorus content grafted onto flax fibers. In addition, the methacrylic monomers showed a strong grafting reactivity compared to the other studied monomers. Self-extinguishing fabrics were obtained when fabrics were modified with MVP and MAPC1 at a concentration of 10 wt% in aqueous solution and irradiated at 50 kGy with a char yield between 17 and 23.5 wt%.

In the present study, flax fibers irradiated under E-beam at different doses (5, 10, 20, 50 et 100 kGy) were treated with MAPC1/water solutions at different monomer concentrations (1, 5 et 10 wt%). MAPC1 was chosen as FR to improve the flame retardancy of flax by covalent grafting. The effects of radiation dose, monomer concentration, reaction time and temperature on the FR grafting rate were investigated. The influence of the pre-irradiation grafting of MAPC1 on the flame retardancy of flax fibers was studied and the results were compared with previous works obtained for simultaneous radiation grafting process.

2. Experimental part

2.1. Materials

Flax fabrics were provided by Hexcel (France). with a chemical composition of 81 wt% of cellulose, 13 wt% of hemicelluloses and 2.7 wt% of lignin [16]. Fabric weight is 200 g/m².

Dimethyl(methacryloyloxy)methyl phosphonate (MAPC1) (**Figure 1**) was purchased from Specific Polymers (Castries, France) and used as received without any purification.

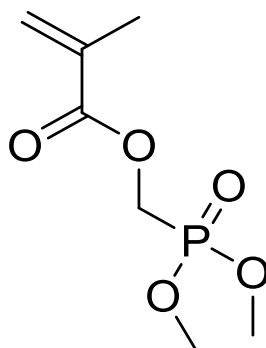


Figure 1 : Chemical structure of MAPC1.

2.2. Grafting procedure

Pre-irradiation grafting process was carried out in three main steps: irradiation, impregnation and washing step of flax fabrics.

In the first step, flax fabrics were irradiated at radiation doses of 5, 10, 20, 50 and 100 kGy in air, at room temperature, using an electron beam accelerator (energy 9.8 MeV, power 27 kW) by Ionisos SA (Chaumesnil, France). The irradiated samples were immediately cold stored to preserve the free radicals hence formed.

In the second step, an impregnation solution was prepared containing 10 wt% of MAPC1 and 90 wt% of deionized water. In order to study the influence of monomer concentration on the grafting, other MAPC1 concentrations were tested: 1 wt% and 5 wt%. The mixture was placed under bubbling argon for 15 min in order to remove oxygen from the reaction medium. Then, samples of irradiated flax fabrics ($3 \times 3 \text{ cm}^2$) were immersed in the impregnation solutions (a fabric/solution weight ratio of 1/100 was fixed for all the tests) without stirring at 80°C or at room temperature for variable times: 5 min, 10 min, 20 min, 30 min, 1h30, 2 h, and 24 h. Finally, the treated fibers were washed three times with deionized water (30 ml per wash) at room temperature to remove unreacted monomer and free polymer chains which were not covalently bonded to the flax structure. The washed fabrics were then placed under a fume hood until total removal of water.

In order to validate the effectiveness of the pre-irradiation procedure, a reference sample of unirradiated flax, which has undergone the same operating conditions, was prepared. Different parameters have been monitored such as the radiation dose, the concentration of monomer in the impregnation solution, the grafting temperature. In this article, the different samples are named according to the following code: F-100kGy-MAPC1 (10 wt%/80°C/24 h) for flax fibers irradiated at 100 kGy and treated with 10 wt% MAPC1 at 80°C for 24 hours.

2.3. Characterization

2.3.1. Electron Paramagnetic Resonance (EPR)

EPR experiments were performed on a Bruker Elexsys E500 spectrometer equipped with a Bruker SHQ EPR cavity. Glass NMR (Nuclear Magnetic Resonance) tubes were filled with known quantities (typically 30-40 mg) of irradiated flax fibers (1 to 100 kGy). NMR tubes were introduced in EPR cavity and spectra were recorded (Records settings: Sweep Time 61s, Sweep Width 200G, Gain 60db (Attenuation), Mod. Amp. 1.0 G, Conv. Time 6 ms, Mod. Freq. 100 kHz). Signal intensities are obtained by double integration (arbitrary unit).

For monitoring at 80°C the EPR signal of flax fibers irradiated at 100 kGy as a function of time for a period of 9 hours, 30 mg of fibres were introduced in a glass NMR tube and inserted into the EPR cavity fitted with a Dewar allowing a temperature control (Records Settings: Sweep Time 10s, delay between records $\cong 30 \text{ s}$, Sweep Width 200G, Gain 60db (Attenuation), Mod. Amp. 1.0 G, Conv. Time 9.7 ms, Mod. Freq. 100 kHz). Signal intensities over time are obtained by double integration (arbitrary unit).

2.3.2. 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 2 cm^{-1} .

2.3.3. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

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

2.3.4. Scanning Electron Microscope coupled with Energy Dispersive X-ray spectrometer SEM-EDX

A scanning electron microscope (FEI Quanta 200) was used to obtain fiber section micrographs. The samples were prepared using a single edge blade and the micrographs were obtained using a vertical sample holder under high vacuum at a voltage of 12.5 kV and a working distance of 10 mm. The SEM was coupled with an energy dispersive X-ray spectroscopy, EDX, (Oxford INCA Energy system) which was used to locate the phosphorus in the flax fibers.

2.3.5. Thermogravimetric analysis (TGA)

TGA was performed using thermogravimetric analyzer instrument (Setaram Setsys). Samples (10 mg \pm 1mg) were heated in alumina ceramic crucibles from 30 to 1000 °C at a heating rate of 10 °C/min under nitrogen atmosphere (40 ml/min) with an isotherm at 100 °C for 15 min in order to remove water from the sample. Residual weight at 1000 °C (Res_{1000}), maximum degradation temperature (T_{deg}) (i.e. temperature of the mass loss rate peak) and maximum peak of mass loss rate (pMLR) were determined.

2.3.6. Pyrolysis combustion flow calorimetry (PCFC)

A pyrolysis combustion flow calorimeter (Fire Testing Technology Ltd., UK) was used to investigate the fire behavior of samples at microscale (2-4 mg). Sample pyrolysis was performed at a heating rate of 1 °C/s under a nitrogen flow (100 ml/min) from 80 to 750 °C (anaerobic pyrolysis – method A according to the standard ASTM D7309). Pyrolysis gases were carried to a combustor in the presence of a N_2/O_2 (80/20) mixture. In such conditions, all gases were fully oxidized. Heat Rate Release (HRR) was calculated according to Huggett's relation which states that 1 kg of consumed oxygen corresponds to 13.1 MJ of released energy. In our study, each test on a single sample was performed twice to ensure the reproducibility of our measurements. The peak of heat rate release (pHRR), the temperature at pHRR (T_{max}), the total heat release (THR) and the char content were determined.

2.3.7. Preliminary fire test on fabrics

An unstandardized fire test was carried out to assess the flammability of some fabrics. Briefly small pieces of fabrics (around 0.5g) were pinched between two glass plates and maintained vertically. A lighter was used to ignite the top of fabrics. This device allowed assessing if the fabric is self-extinguishing. The residue was also weighed after complete burning (for self-extinguishing fabric, complete burning was reached by multiple flame applications).

3. Results and discussion

3.1. Irradiation of flax fabrics

EPR analysis was used to determine the presence of free radicals on air-irradiated flax fibers before MAPC1 grafting. According to the literature, free radicals must be mainly formed during electron beam irradiation either by abstraction of hydrogen from a glucose moiety, or by cleavage of a glycosidic bond, followed by other degradation processes [26]. On the other hand, the radicals formed by these decomposition reactions of the components of the natural fibers could be transformed into hydroperoxide or peroxide species in presence of oxygen. Moreover, it has been observed that the thermal decomposition of these peroxide groups makes it possible to initiate grafting reactions. Cotton fabrics irradiated in air at room temperature by gamma rays ^{60}Co showed EPR signals which have been mainly attributed to the presence of peroxy radicals, with low contribution from other radical species [27].

According to Iller et al. [28] three types of radical sites have been identified in Kraft softwood pulp structure: (1) reactive sites located on the surface, (2) sites with limited reactivity placed in less rigid domains (amorphous zone) and (3) sites stable for days at room temperature trapped in the crystalline regions of the cellulose (hydroperoxides and peroxides species).

For our samples, the EPR analysis (**Figure 2**) evidences the presence of free radicals on the irradiated fabrics for doses ranging from 1 kGy to 100 kGy. For non-irradiated flax fibers, a weak EPR signal appears (designated as background noise (BGN)). The origin of this signal may be assigned to stable radicals pre-existing in the fibers or created by chemical treatments during the manufacture of the fabrics. [29]

It is observed that the intensity of the EPR signals increases with the increase of the absorbed dose, meaning that high dose irradiation creates more radicals on the flax fibers. [27]

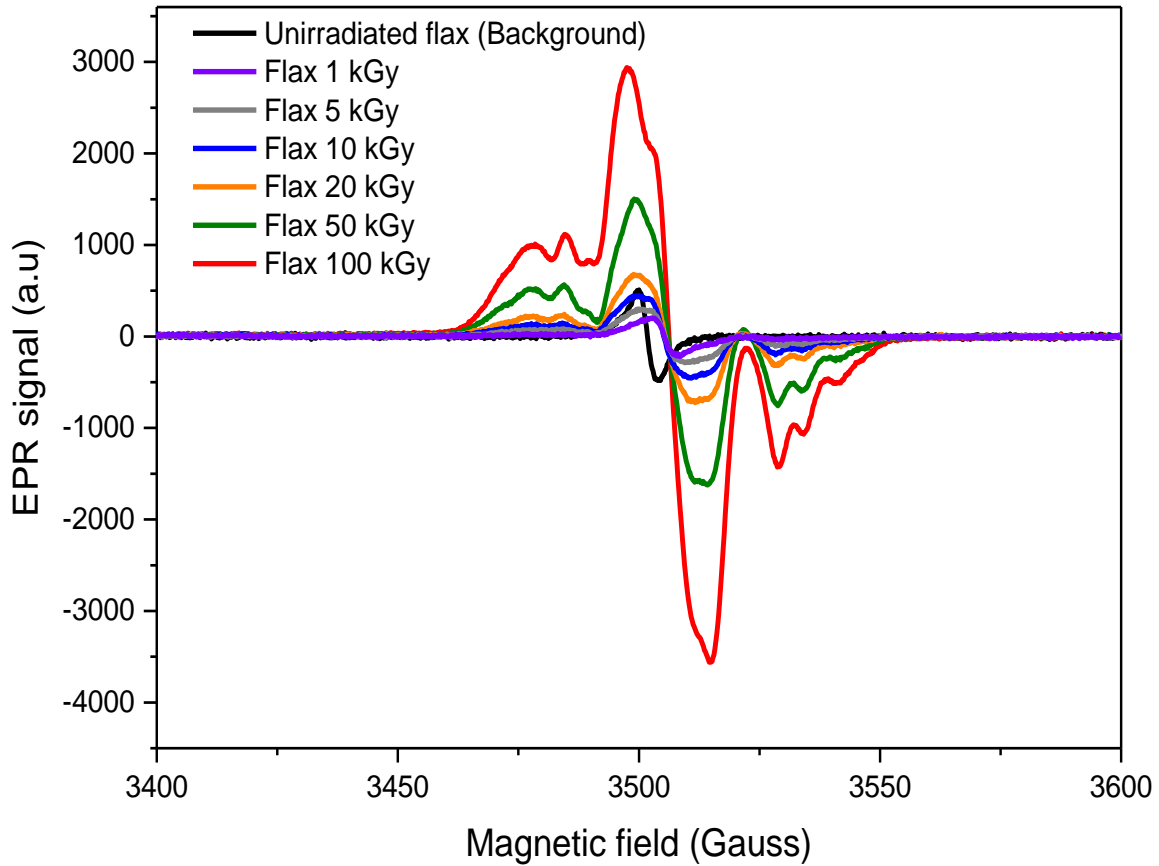


Figure 2: EPR spectra of unirradiated (black spectrum) and irradiated flax fibers at various doses.

Figure 3 represents the evolution of the EPR signal intensity as a function of the radiation dose. The relationship between signal intensity and radiation dose varies linearly over a region extending from a low dose of 1 kGy to a high dose of 100 kGy and takes the following equation already reported in the literature [29]: $S = kD + S_0$

where S and S_0 stand for the signals corresponding to the dose D and from the background noise (BGN), respectively.

These results show that the irradiation allows to easily control the quantity of free radicals created onto flax fibers by choosing the desired dose. The work of Iller et al. [28] proved that the concentration of radicals present in the cellulosic structure increases linearly up to 25 kGy and then more slowly at higher doses due to radiolytic saturation effects, indicating that a maximum concentration of radicals has been reached. This effect is not observed in our case.

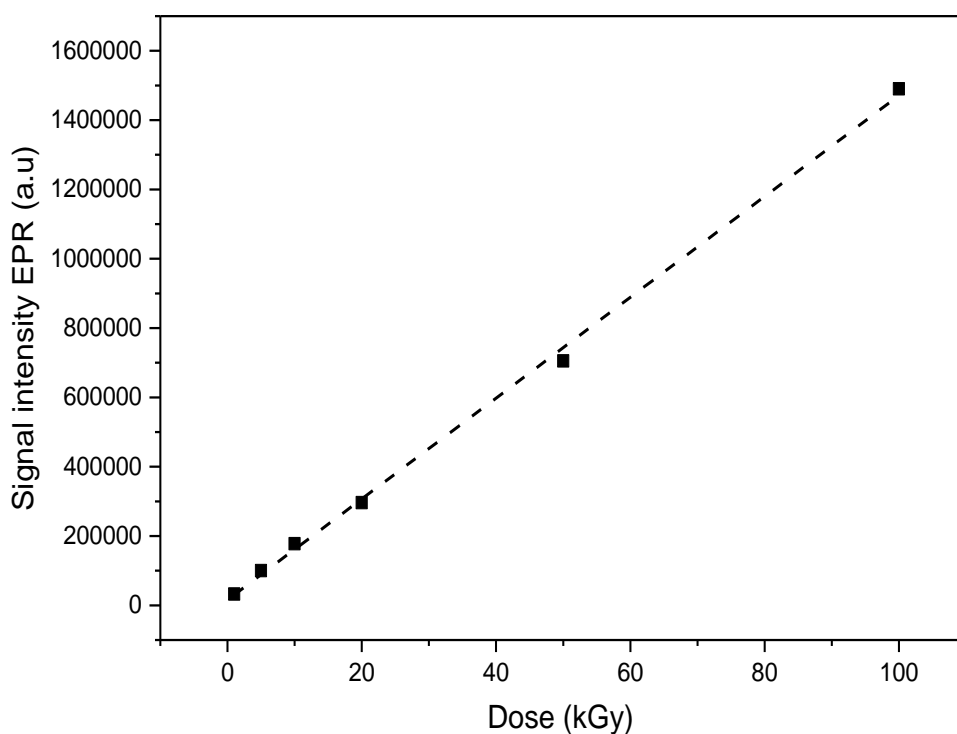


Figure 3: Evolution of the EPR signal of irradiated fibers versus the radiation dose.

Figure 4 shows the measurements carried out on a flax sample irradiated at 100 kGy and then heated to 80 °C during the EPR analysis in order to determine the stability of the radical species created in the fibers after irradiation. The intensity of the EPR signal decreases rapidly after the first few seconds and stabilizes after 2 hours of heating at 80 °C. We also noted that, after 8 hours, the number of radicals present in the fiber remains much higher than in unirradiated fibers (for which the EPR signal intensity almost negligible). This result proves the elimination of free radicals and (hydro)peroxide species present in the irradiated flax when the fibers are heated. The same results were observed at room temperature in the work described by Alberti et al. [26] and Iller et al. [28] with an exponential decrease over time in the intensity of the EPR signal for flax fibres. This decrease was initially rapid and slowed down after the first 12-24 hours, with the intensity reaching a stationary level after 10 days. For this reason, we kept the flax fabrics at low temperature -20 °C after irradiation up to the grafting reaction with MAPC1.

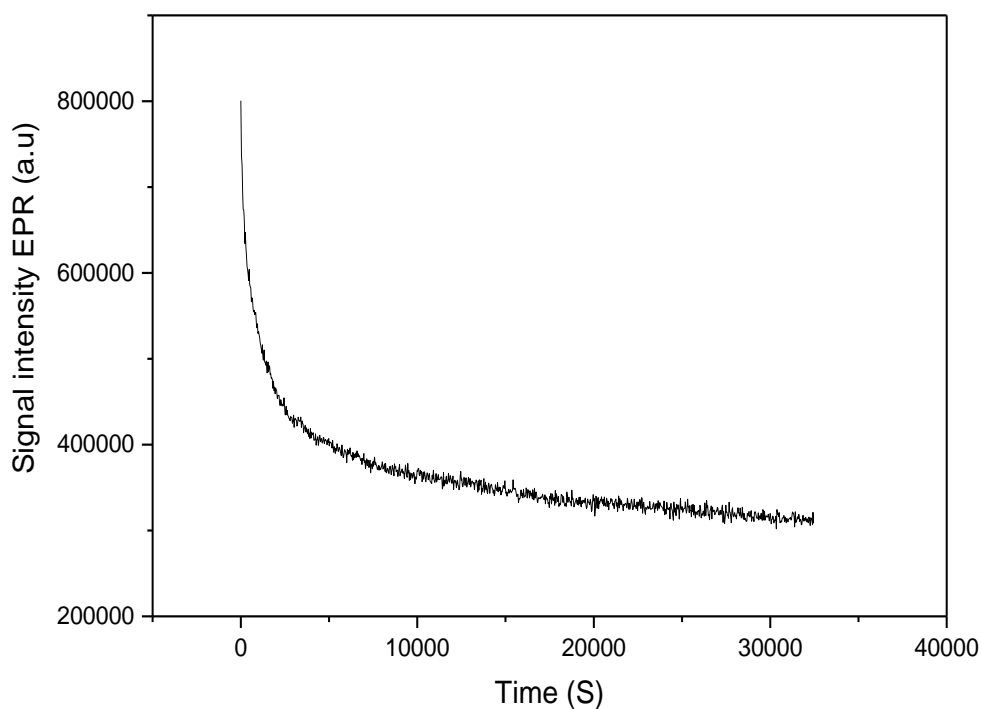


Figure 4: Effect of temperature on the EPR signal from irradiated fabrics.

3.2. Grafting of MAPC1 phosphorus monomer onto the flax fabrics

After the chemical treatment of flax fabrics with the phosphorus flame retardant MAPC1. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis has been used to determine the level of phosphorus grafted on the flax fibers. **Table 1** summarizes the Phosphorus content determined by gravimetry and by ICP-AES of the different prepared samples, specifying the grafting conditions.

Table 1 : Phosphorus content of different samples determined by ICP-AES.

Dose (kGy)	Time (min)	Temperature (°C)	MAPC1 Concentration (wt%)	P% (ICP-AES) (wt%) ^b
0	5	80	10	0.04
	1440	80	10	0.04
5	5	80	10	0.19
	1440	80	10	0.22
10	5	rT	10	0.02
	1440	rT	10	0.23
10	5	80	10	1.35
	10	80	10	2.12
	20	80	10	1.75
	30	80	10	2.05
	90	80	10	1.87
	120	80	10	1.64
	1440	80	10	2.24
	1440	80	5	0.42
	1440	80	1	0.23

50	5	80	10	1.64
	10	80	10	2.16
	20	80	10	1.66
	30	80	10	2.82
	90	80	10	2.02
	120	80	10	2.74
	1440	80	10	2.88
	1440	80	5	1.51
	1440	80	1	0.34
100	5	80	10	2.59
	10	80	10	5.54
	20	80	10	5.34
	30	80	10	6.88
	90	80	10	6.02
	120	80	10	4.50
	1440	80	10	6.97
	1440	80	5	5.15
	1440	80	1	1.50

Different parameters of the grafting reaction were studied in this work to evaluate their influence on the grafting rate and on the phosphorus content in the treated fabrics, namely the radiation dose (**Figure 5**), the FR monomer concentration in the reaction solution (**Figure 6**), the reaction time (**Figure 7**) and temperature (**Table 1**). These parameters make it possible to control the yield of phosphorus monomer grafted onto the flax fibers.

Figure 5 represents the evolution of the phosphorus content *versus* the radiation dose. For a grafting at 80 °C with a FR monomer concentration of 10 wt%, the phosphorus content for 24 hours of reaction increases from 2.24 wt% for a low dose of 10 kGy to 6.97 wt% for a 100 kGy-dose. The same results were observed for MAPC1 concentrations of 1 wt% and 5 wt% from 0.23 wt% to 1.5 wt% and from 0.42 wt% to 5.15 wt%, respectively (**Figure 5a**). Moreover, a very slow tendency leading to a pseudo plateau was noted for low doses ranging between 10 kGy and 50 kGy and especially for a highest FR concentration of 10 wt% regardless the reaction time (**Figure 5b**). For a high dose in the range of 50 and 100 kGy, the phosphorus content increases rapidly to reach 1.50 wt%, 5.15 wt% and 6.97 wt% for MAPC1 concentrations of 1, 5 and 10 wt%, respectively. These results confirm that higher absorbed doses lead to formation of a greater number of free radicals in the fabrics. Consequently, more free radicals are available to initiate the polymerization reaction of MAPC1 in the flax fibers. This trend was contrarily to the work of Sekine et al. [21] who noted that the degree of grafting of GMA onto non-woven cellulose fibers monotonously increased with increasing absorbed doses and reached 280% at 50 kGy. The same tendency was observed by Jordan et al. [19] who reported that the GMA degree of grafting onto water hyacinth increased with absorbed dose in the range 5 kGy-20 kGy and stabilized above 20 kGy.

In addition, polymerization at room temperature resulted in insignificant levels of phosphorus as shown in **Table 1**. For a 10 kGy-dose and a monomer concentration of 10 wt%, a phosphorus level of 0.02 wt% is

reached after 5 minutes, while after 24 hours, a phosphorus content of 0.23 wt% was obtained. These results prove that a thermal activation (i.e. grafting at 80 °C) was required to increase the degree of grafting.

In addition, the influence of the MAPC1 concentration in the reaction solution on grafting efficiency is shown in **Figure 6**. A linear correlation is observed between the grafted phosphorus levels and the FR concentration in solution especially at 50 and 100 kGy. This tendency has been also observed in previous work. [15,17] For irradiated fabrics at 100 kGy, the phosphorus content evolves from 1.50 to 6.97 wt% when monomer concentration increased from 1 to 10 wt%. On the other hand, for fibres irradiated at 50 and 10 kGy, the phosphorus contents increased from 0.34 wt% to 2.88 wt% and from 0.23 wt% to 2.24 wt% when the monomer concentrations increased from 1 wt% to 10 wt%, respectively. These results prove that controlling the monomer concentration is an easy way to tune the final phosphorus content in fibers (keep in mind that the flame retardancy is primarily dependent on the phosphorus content) and a dose of 10 kGy seems to be sufficient to achieve high levels and to avoid any degradation of fabrics typically noted at high doses. In addition, **Figure 7** represents the evolution of the phosphorus content versus the grafting time ranging from 5 min to 24 hours, where the phosphorus content was not increased continuously during the grafting reaction. For the 10 and 50 kGy doses, the Phosphorus level slowly increases in the first 30 min of grafting to reach 2.05 wt% and 2.82 wt%, respectively. In the same interval of reaction time (0 to 30 min), a fast increase of phosphorus content in fibers irradiated at higher doses (100 kGy) was observed to achieve a level of 6.68 wt%. However, for intermediate reaction times of 90 to 120 min, a slight drop was noted for all three doses. We assume that the evolution of the phosphorus content with reaction time is probably due to a limited loss of the phosphorus polymer grafted onto extractables of the flax fibers. These components could be eliminated progressively in the first part of the polymerization due to the heating at 80°C in water. For the maximum reaction time of 24 hours and whatever the irradiation dose applied, the phosphorus content tends to re-increase to significant values of 2.24 wt%, 2.88 wt% and 6.97 wt% for doses of 10, 50 and 100 kGy, respectively. After removing extractables, the structure of flax becomes stable and the polymerization of the phosphorus monomer again increases the phosphorus content. A different tendency was noted by Moawia et al. [30] with a rapid increase in the grafting rate in the first hour after which the reaction slowed down and the grafting stabilized to reach saturation after 4 hours. In addition, Sharif et al. [22] showed the same evolution of the grafting rate versus time, with a rapid increase after 3 hour-reaction followed by a stabilization. ICP-AES analysis were also performed on unirradiated flax fibers and treated with phosphorus monomer under the same conditions, an almost negligible phosphorus content was obtained with a value of 0.04 wt%.

In conclusion, in order to achieve maximum levels of phosphorus grafted onto the fibers, the radiation dose, the reaction time and temperature, and the FR monomer concentration may be increased while maintaining suitable conditions to avoid the flax degradation. These results are in good agreement with those obtained by Hajj et al. [15] for the grafting of different phosphonated monomers on flax fibers using simultaneous grafting method. In the case of MAPC1 monomer, 1.06 wt% was grafted onto flax fibers when the FR concentration in aqueous solution was set at 10 wt% for an irradiation dose of 50 kGy. The authors observed that the degree of

grafting of phosphonated monomers onto flax fibers increased with the absorbed dose and the monomer concentration.

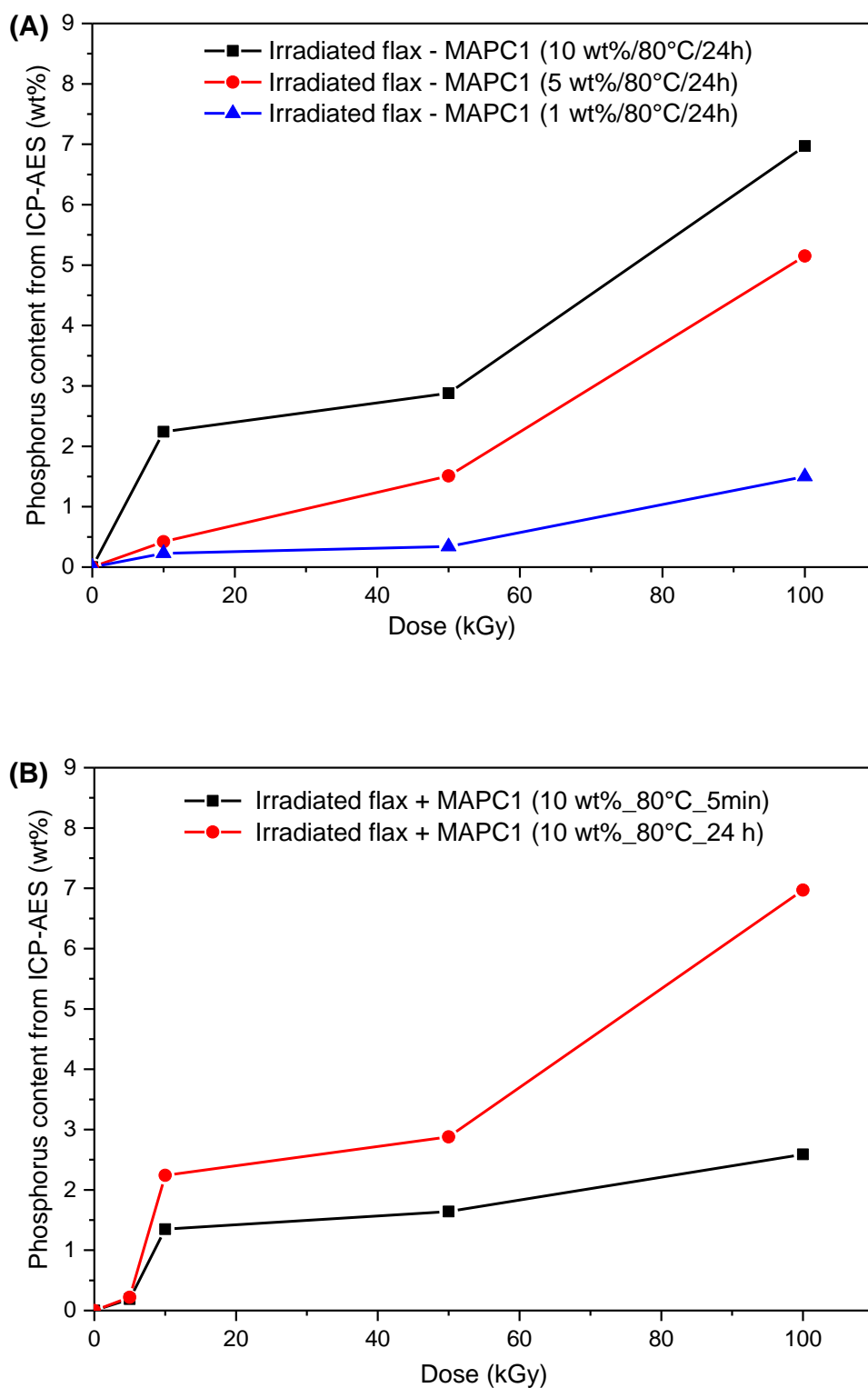


Figure 5 : Effect of radiation dose/monomer concentration (A) and radiation dose/reaction time (B) on the pre-irradiation grafting of MAPC1 at 80°C.

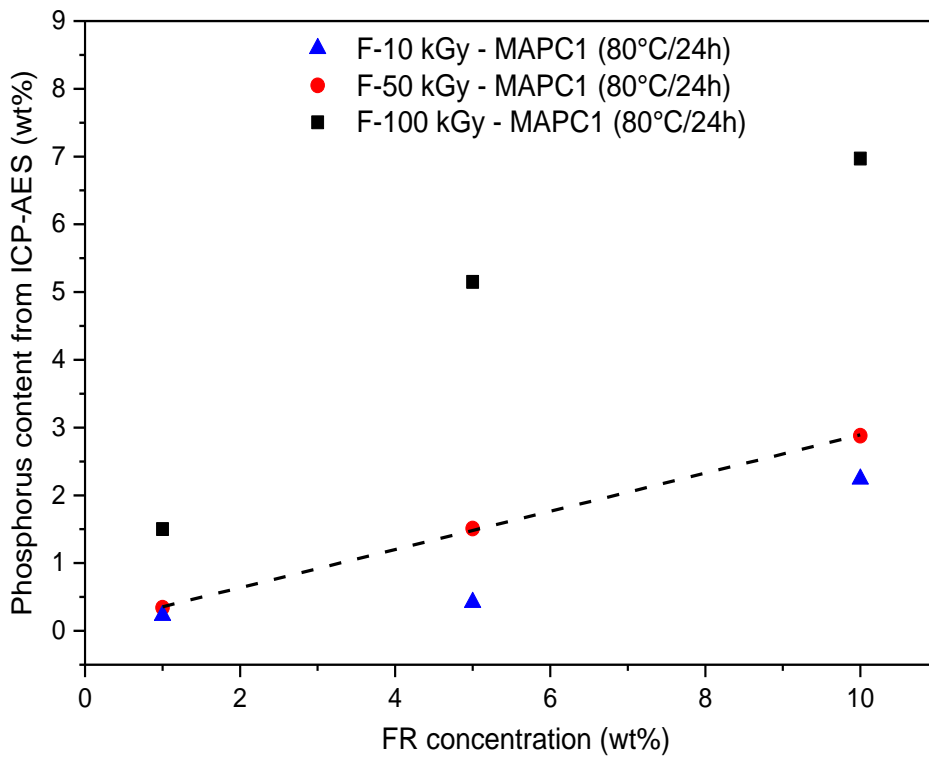


Figure 6 : Phosphorus content (from ICP-AES) versus MAPC1 concentration in solution (wt%) at various doses.

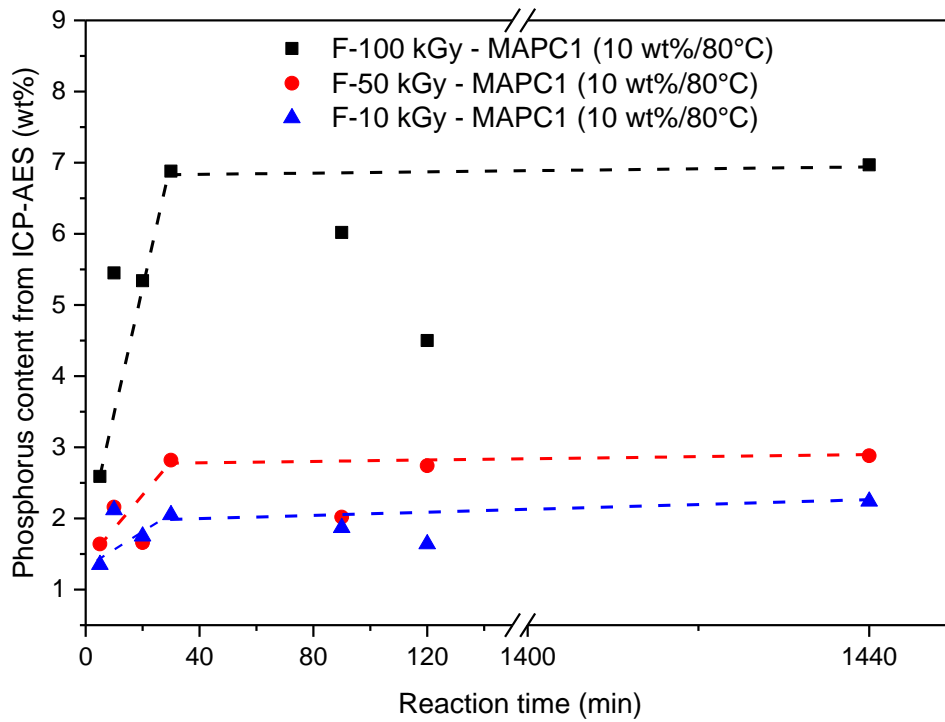


Figure 7: Effect of the reaction time on the phosphorus content (ICP-AES): dose 10, 50 and 100 kGy, 10 wt% MAPC1, $T = 80^{\circ}\text{C}$ (dotted lines are guidelines for eyes).

The grafting of the MAPC1 monomer onto flax was confirmed by Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscope coupled with Energy Dispersive X-ray spectrometer (SEM-EDX). The FTIR spectra were recorded on irradiated flax fibers at 100 kGy treated with phosphorus monomer and on unirradiated flax fibers for comparison purpose. The spectrum obtained for irradiated fibers treated with MAPC1 (**Figure 8**) reveals the presence of three new bands attributed to the phosphorus monomer: i) an intense frequency at 1740 cm^{-1} assigned to $\text{C}=\text{O}$ in the ester group, ii) a band at 1250 cm^{-1} corresponding to the elongation of the $\text{P}=\text{O}$ function and iii) a characteristic deformation frequency of the $\text{P}-\text{O}-\text{C}$ bonds at 790 cm^{-1} [31,32]. The presence of these signals for the various tested doses confirms the efficiency of the grafting of MAPC1 onto flax fibers, even for low irradiation doses.

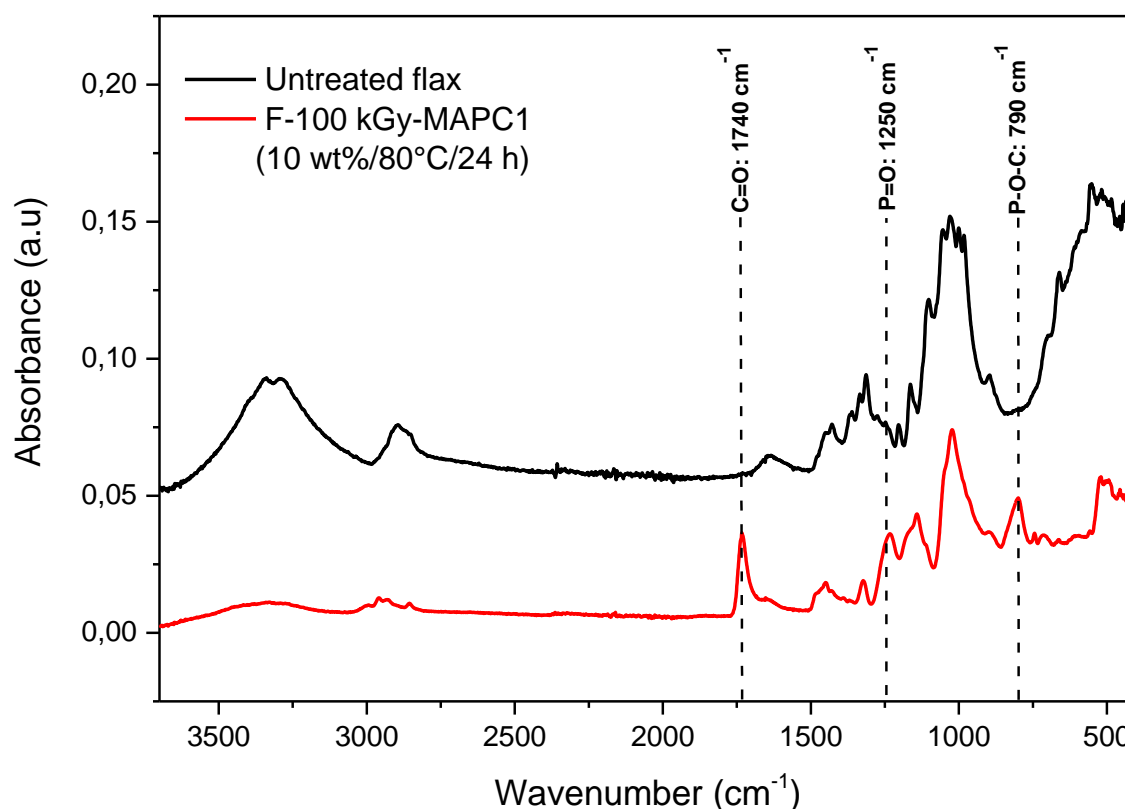


Figure 8: FTIR Spectra of untreated (black) and irradiated flax fibers treated with MAPC1 (100kGy_10 wt%_80°C_24h, red) (normalized by the band at 1202 cm^{-1}).

SEM-EDX analyses were performed to evaluate the chemical composition of modified flax fabrics and to define the distribution of chemical elements in the section of elementary fibers.

Phosphorus mapping for the flax fibers irradiated and treated with MAPC1 (10 wt% in water) at 80°C shows that the phosphorus is homogeneously located from the surface to the bulk of the elementary flax fibers

whatever the dose and the reaction time (**Figure 9**). Same results are observed for irradiation dose of 10, 20, 50 and 100 kGy when fibers were treated with 10 wt% MAPC1 solution at room temperature (**Figure 10**). On the other hand, in the case of the unirradiated fabric (0 kGy) having undergone the MAPC1 treatment (**Figure 9b and Figure 10b**), the SEM-EDX analysis does not display any significant presence of phosphorus, with an almost negligible rate of about 0.2 wt%. This very low rate is attributed to residual traces of MAPC1 monomer remaining after the various washes or to the possible phosphorus naturally present in natural fibers. In a previous work, Sonnier et al. [16] reported for simultaneous grafting method that when a 10 wt% MAPC1/THF solution was used for the impregnation step, phosphorus is only located on the surface of elementary flax fibers. The authors noted there was no significant grafting of MAPC1 into the bulk of elementary flax fibers, which resulted in a low phosphorus rate of 0.34 wt%. While for dimethyl vinylphosphonate (MVP) monomer, they evidenced that phosphorus element was also present into the bulk with a high content (~ 4 wt%). On the other hand, Hajj et al. [15] proved that the simultaneous grafting of MAPC1 (10 wt% FR/Water) onto flax fibers, irradiated at 50 kGy, results in a significant phosphorus content of 1.06 wt%.

The results of our study indicate that the pre-irradiation method leads to higher phosphorus content even at low radiation dose compared to the simultaneous grafting. Moreover, the irradiation at low dose (10 kGy) and a very short reaction time (5 min), which prevents degradation of flax fibers, are sufficient to achieve a high level of grafting and a homogeneous distribution of phosphorus within the fiber section.

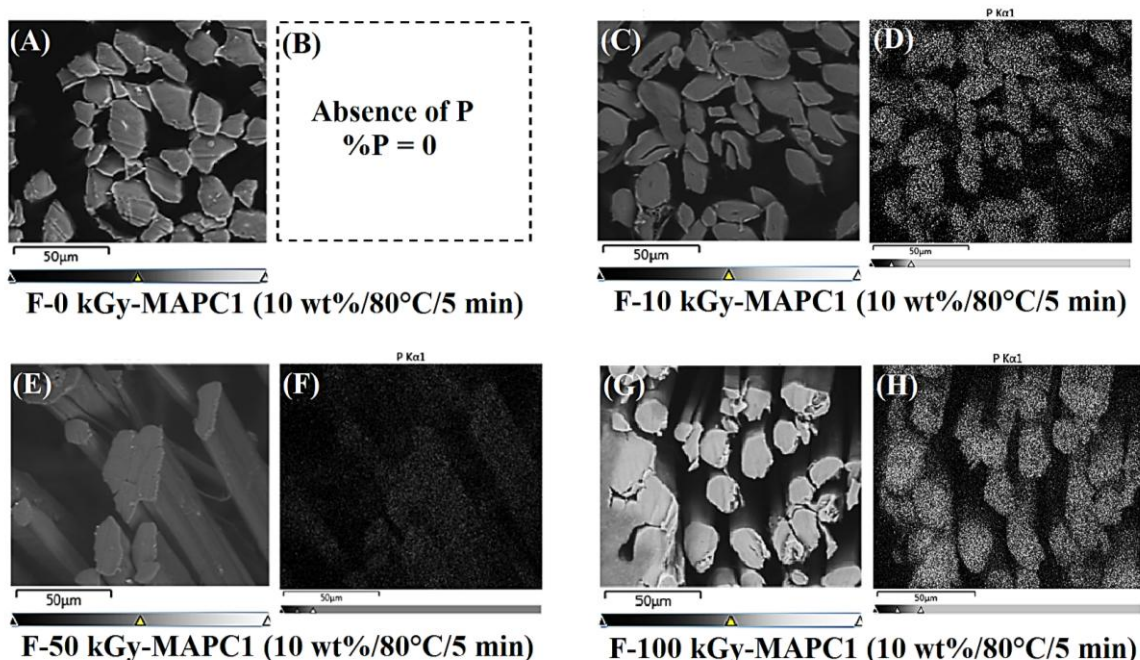


Figure 9: EDX phosphorus mapping of flax fabrics unirradiated (B)/ irradiated (D), (F), (H) at different doses and treated by 10 wt% MAPC1 aqueous solutions at 80°C.

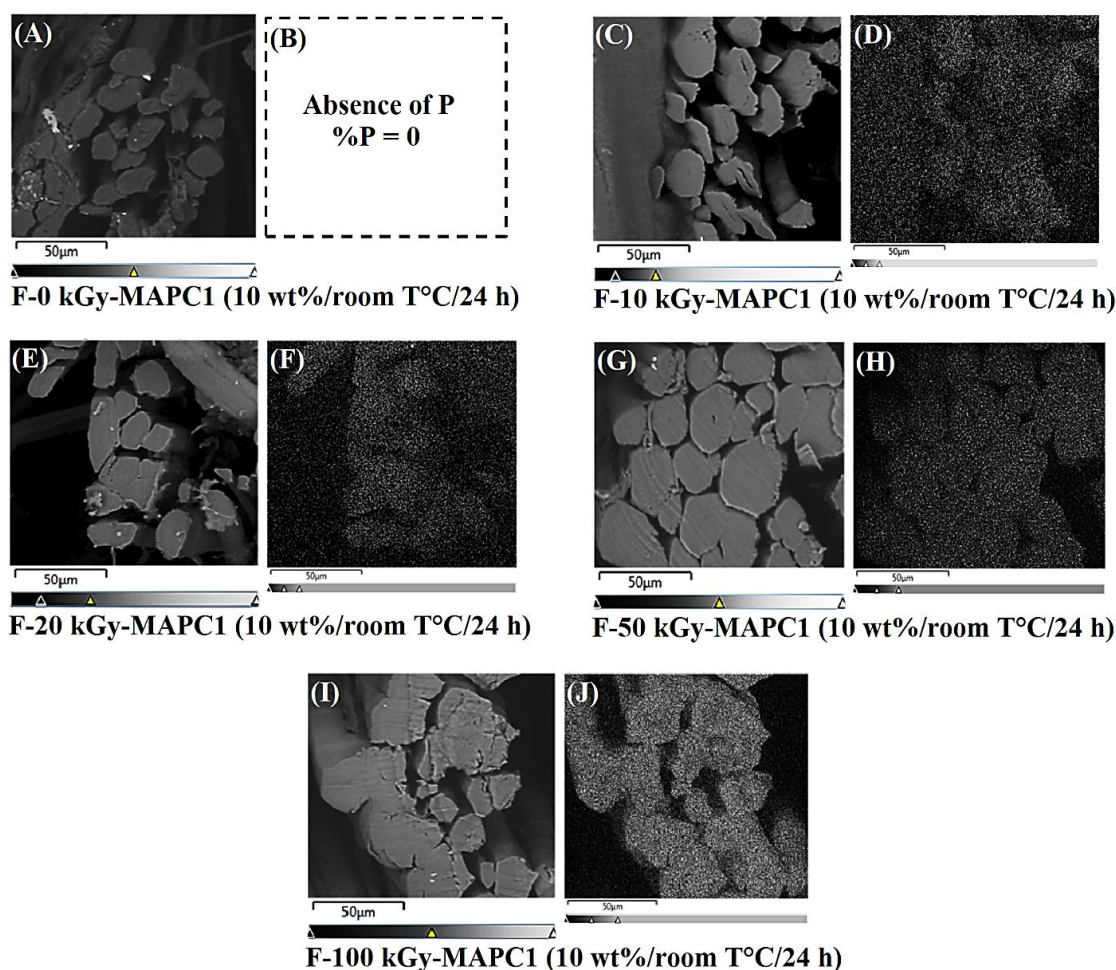


Figure 10: EDX phosphorus mapping of flax fabrics unirradiated (B)/ irradiated (D), (F), (H), (J) at different doses and treated by 10 wt% MAPC1 aqueous solution at room temperature.

3.3. Phosphorus effect on fibers flammability

Flame retardancy and thermal degradation of the modified flax fibers were assessed by pyrolysis combustion flow combustion flow calorimetry (PCFC) and thermogravimetric analysis (TGA). The heat release rate (HRR) curves for the different samples, untreated and treated with MAPC1, are gathered in **Figure 11** and main data are listed in **Table 2**. For unirradiated and untreated flax fibers, the peak of heat release rate (pHRR) occurs at about 370 °C with a value of about 230 W/g. Total heat release (THR) is close to 9 kJ/g in good agreement with previous works. [14,15].

Grafting MAPC1 onto irradiated flax fibers at 100 kGy with polymerization at 80 °C for 5 min (**Figure 11a**) led to sharp decreases in both pHRR (from 230 W/g to 58 W/g) and pHRR temperature (from 370 °C to 260 °C). The THR value was also reduced to 3.7 kJ/g and the char residue was increased to 35 wt% (whereas the residue for the untreated fibers is 11 wt%). In addition, polymerization at 80 °C for 24 hours (**Figure 11b**) yields to similar results with a pHRR of 73 W/g, a pHRR temperature of 244 °C, a THR of ca. 2.9 kJ/g and a high char content of 40 wt%. Flame retardancy properties were also observed for the samples irradiated and treated with 10 wt% of phosphorus monomer at room temperature despite a lower phosphorus content (**Figure 11c**). For a 10 kGy-dose, the pHRR decreases from 230 W/g to 86 W/g, THR also decreases to 4.4 kJ/g while

char residue increased to 29 wt%. The main PCFC data are plotted versus phosphorus content in **Figure 12**. The intensity of pHRR decreased systematically from 230 W/g to 61 W/g (**Figure 12a**) when phosphorus content increased. The pHRR temperature decreased from 370 °C to 240 °C due to an early decomposition of the cellulose (**Figure 12b**). Concomitantly, THR decreased (from 9.0 kJ/g to 2.5 kJ/g) because carbon was partially trapped into the condensed phase (**Figure 12c**). Additionally, the THR value tends to slightly increase at higher phosphorus levels (between 5 and 7 wt%) due to the excess of MAPC1 present in the treated fibers. Indeed, the own contribution of MAPC1 to heat release rate is not negligible (11.4 kJ/g) [32]. Moreover, the char content increases from 10 wt% to around 40wt% (**Figure 12d**). These results can be explained by the fact that with increasing temperature, the phosphorus flame retardant decomposes, leading to the formation of phosphoric acid, which may induce a phosphorylation of the primary hydroxyl group of cellulose to form a phosphorus ester. These esters catalyze the dehydration of cellulose at low temperature, promoting the formation of char [33]. Thus, charring is assisted by the presence of phosphorus, leading to higher residue yield and lower THR and decreased thermal stability compared to untreated flax fibers. A rapid evolution of the main data for phosphorus levels between 1 and 2 wt% has also been observed while at higher phosphorus content, ranging from 2 to 7 wt%, a very slow progression was identified. All these results are in agreement with those obtained by Hajj et al. [14,15] for simultaneous grafting.

Table 2 : Main data from PCFC for untreated and treated flax fibers by MAPC1 grafting

	[MAPC1] (wt%)	Temperature (°C)	Time (min)	PCFC					TGA
				P content (wt%)	pHRR (W/g)	Temperature pHRR (°C)	THR (kJ/g)	Residue (wt%)	Residue at 1000 °C (wt%)
Untreated flax fiber	-	-	-	0	230	370	9.0	11	2.18
F-5kGy-MAPC1	10	80	5	0.19	104	315	6.5	22	7.61
	10	80	1440	0.22	133	324	6.8	24	-
F-10kGy-MAPC1	10	80	5	1.35	75	300	4.8	30	13.23
	10	80	10	2.12	69	254	3.5	34	-
	10	80	20	1.75	71	273	3.9	27	-
	10	80	30	2.05	78	299	4.4	26	-
	10	80	90	1.87	63	286	3.8	28	-
	10	80	120	1.64	65	256	3.5	37	-
	10	80	1440	2.24	75	252	3.5	33	20.17
	5	80	1440	0.42	107	316	5.8	23	12.51
	1	80	1440	0.23	175	324	8.1	16	9.23
F-10kGy-MAPC1	10	rT	5	0.02	172	314	7.5	19	-
	10	rT	1440	0.23	86	285	4.4	29	10.20
F-50kGy-MAPC1	10	80	5	1.64	65	255	2.8	32	11.25
	10	80	10	2.16	60	246	3.1	33	-
	10	80	20	1.66	85	258	3.6	36	-
	10	80	30	2.82	83	242	3.7	35	-
	10	80	90	2.02	64	245	3.6	35	-
	10	80	120	2.74	61	241	3.3	34	-

	10	80	1440	2.88	63	249	2.6	43	-
	5	80	1440	1.51	90	303	4.8	25	13.31
	1	80	1440	0.34	276	328	10.8	9	2.58
F-100kGy-MAPC1	10	80	5	2.59	58	260	3.7	35	19.22
	10	80	10	5.45	72	259	3.8	38	-
	10	80	20	5.34	74	255	3.8	38	-
	10	80	30	6.88	62	258	4.3	34	-
	10	80	90	6.02	65	253	4.6	36	-
	10	80	120	4.50	104	244	3.4	33	-
	10	80	1440	6.97	73	243	2.9	40	24.75
	5	80	1440	5.15	56	246	2.8	41	19.06
	1	80	1440	1.50	52	278	3.4	33	15.49

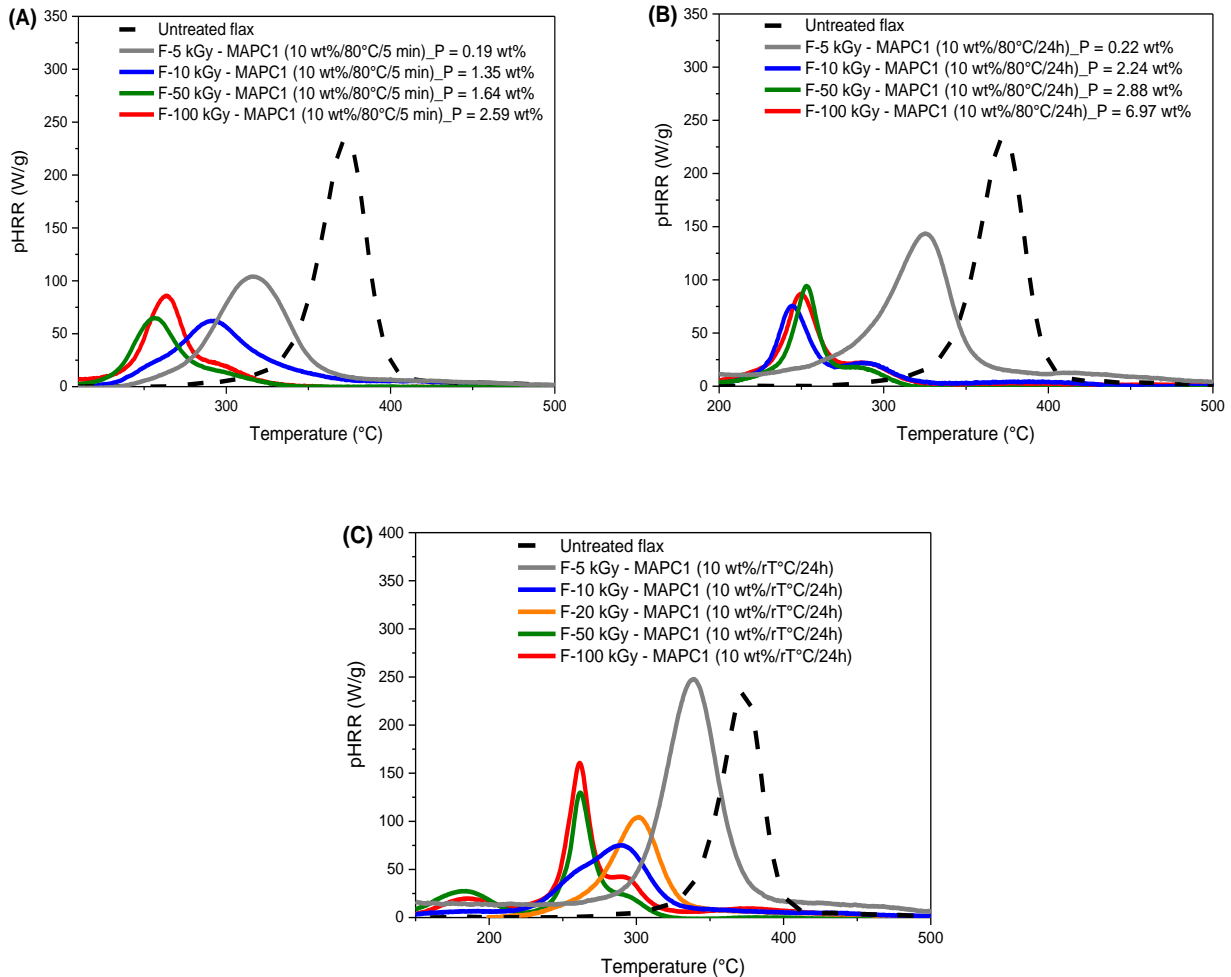


Figure 11: HRR curves of various pre-irradiated and treated flax fibers with 10 wt% MAPC1 in PCFC (anaerobic pyrolysis). (A) Polymerization at 80 °C for 5 min, (B) Polymerization at 80 °C for 24h, (C) Polymerization at room temperature for 24 h.

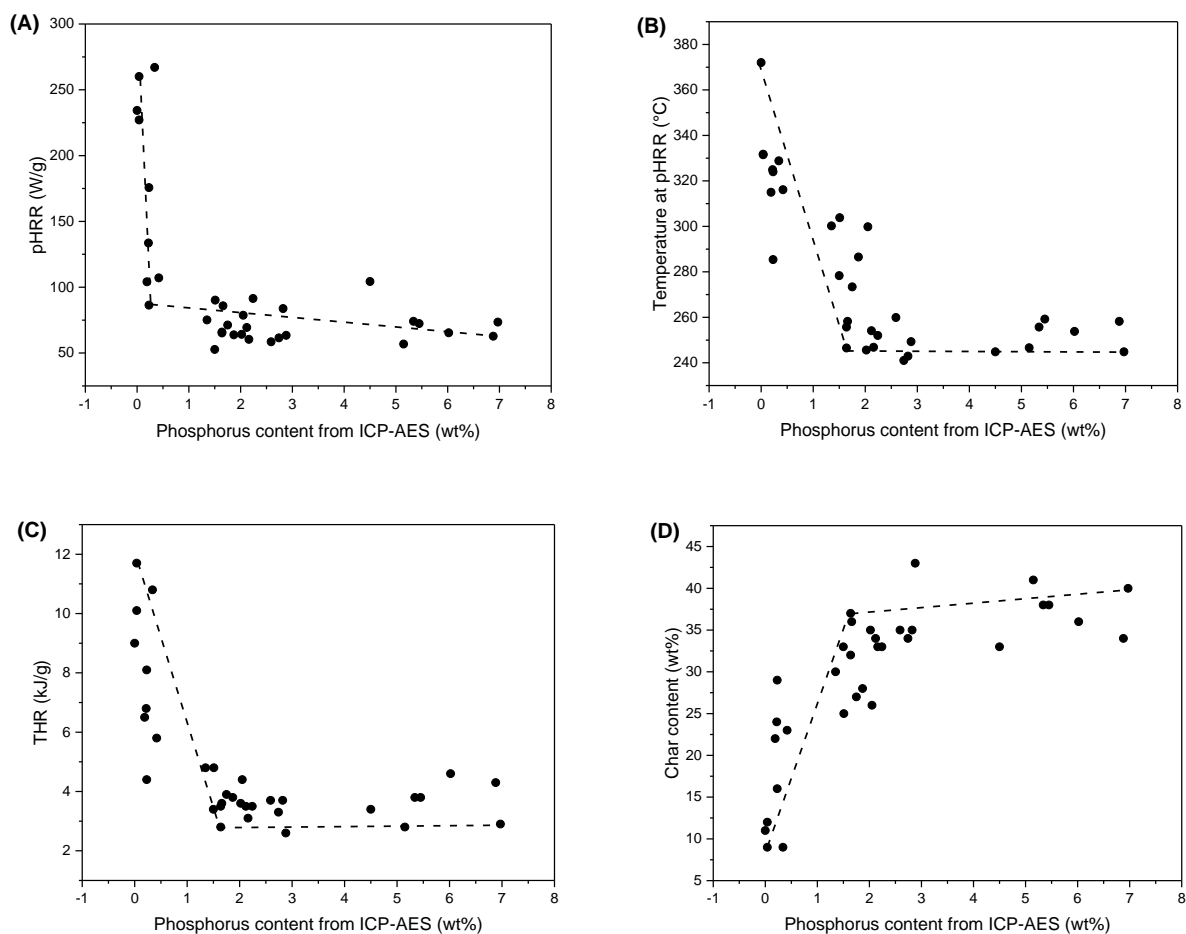


Figure 12: Effect of phosphorus content in the modified flax fabrics on (A) pHRR, (B) temperature at pHRR, (C) THR and (D) Char content from PCFC analysis (dotted lines are guidelines for eyes).

The thermal stability of such materials was also studied by thermogravimetric analysis. As seen above, a high radiation dose and a high monomer concentration in the impregnation solution lead to higher phosphorus content on the modified fibers. According to **Figure 13**, it can be seen that at high phosphorus levels, fabric degradation starts at lower temperatures while the residue level at 1000 °C increases. The temperature decreases from 365 °C to 250 °C with a residue increase from 2.2 wt% to 24.8 wt% for untreated and treated fibers (F-100kGy-MAPC1(10 wt%/80°C/24h) _ P = 6.97 wt%), respectively (**Figure 13a**). The same evolution was observed for modified flax irradiated at low doses (F-10kGy-MAPC1 (10 wt%/80°C/24h) _ P = 2.24 wt%) (**Figure 13b**) with a degradation temperature of about 280 °C and a high residue yield of 20.2 wt%. For different radiation doses and the same phosphorus content (0.20 wt%, **Figure 13c**), the residue level at 1000 °C is almost identical e.g. for samples irradiated at 5 kGy and 10 kGy, the degradation temperature is about 300 °C with an almost similar residue yield of 7.9 wt% and 9.2 wt%, respectively. This highlights that the major factor controlling the degradation of treated fibers is the content of grafted phosphorus FR.

Overall, the flammability at the micro-scale is mainly impacted by the phosphorus content (**Figure 14**). The results indicate the same tendency as that reported in Hajj et al.'s study [15] for the simultaneous grafting.

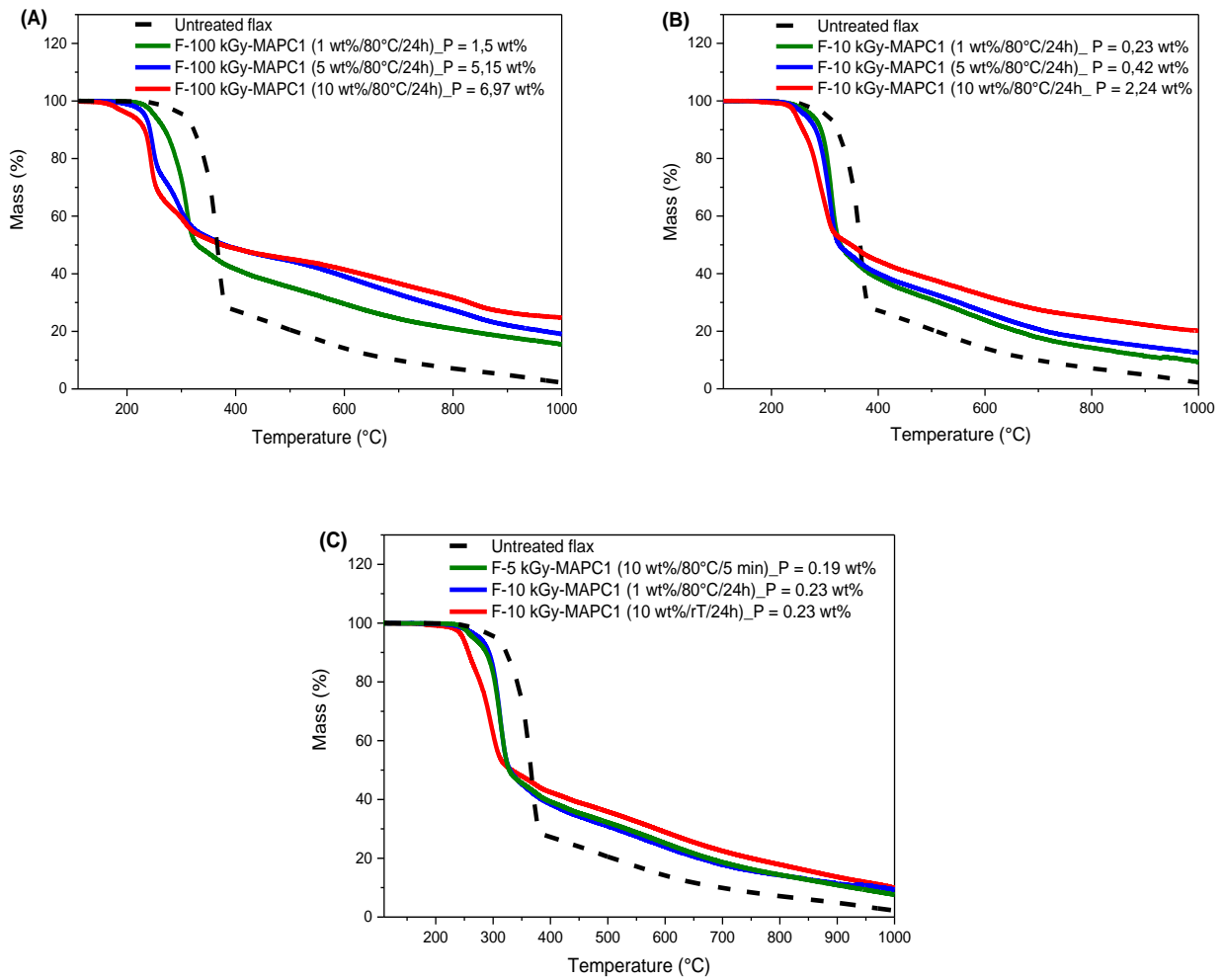


Figure 13: Thermogravimetric curves under N_2 for modified flax fibers irradiated (A) at 100 kGy, (B) at 10 kGy and treated with different FR concentrations: 1, 5 and 10 wt% at 80 °C for 24 h, (C) TGA for samples with the same P content value.

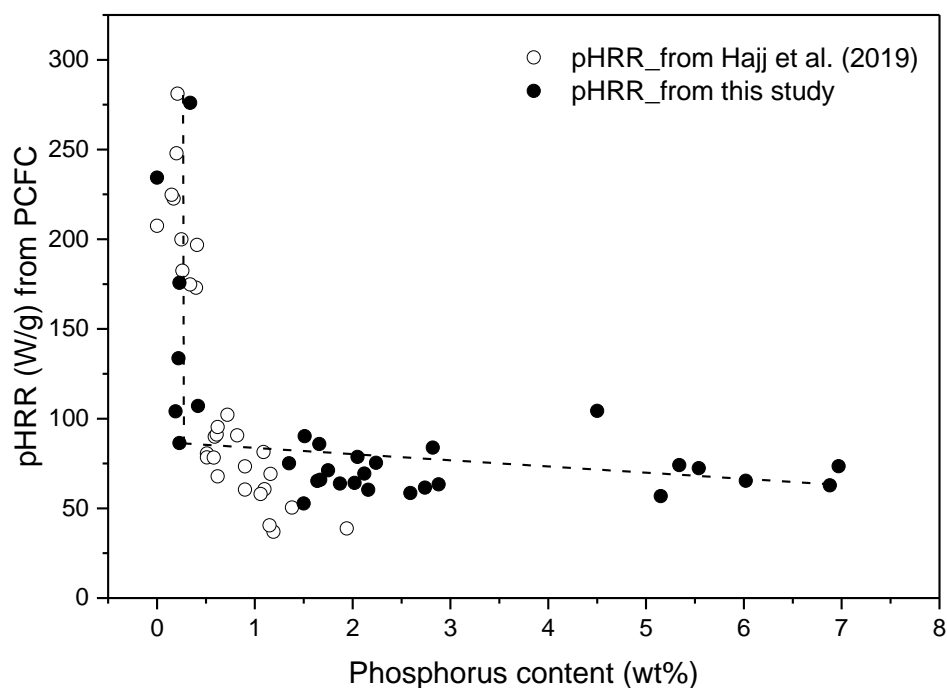
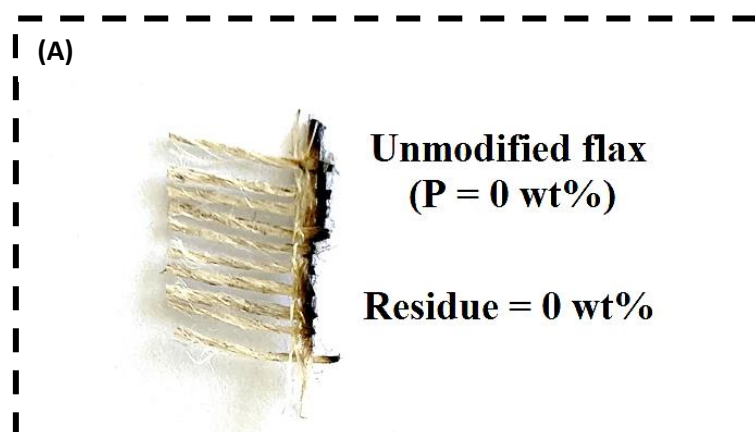


Figure 14: Influence of phosphorus content on pHRR using PCFC (dotted lines are guidelines for eyes).

Preliminary fire tests were carried out on untreated and treated flax fibers to evaluate the effect of the pre-irradiation modification on flame retardancy at small scale (**Figure 15**). Untreated flax fibers (with a negligible phosphorus content) produces a small residue after ignition which is totally degraded in a few seconds due to thermo-oxidation (aerobic pyrolysis after extinction of the flame) (**Figure 15a**). The final char yield in this case is around 0%. The modified fabrics irradiated at 10 kGy (F-10kGy-MAPC1(10 wt%/80°C/24h) – phosphorus content = 2.24wt%) (**Figure 15b**) and at 100 kGy (F-100kGy-MAPC1(10 wt%/80°C/24h) - phosphorus content = 6.97wt%) (**Figure 15c**) revealed a self-extinguishing character with a significant charring content of 34.6 wt% and 53.1 wt%, respectively. These results evidence that the phosphorus FR promotes both the charring and its thermo-oxidative stability.



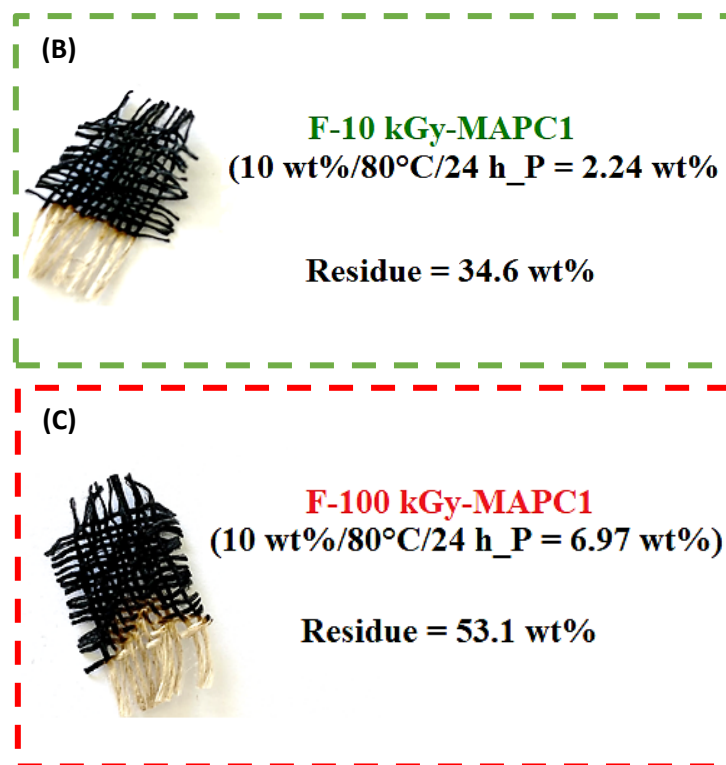


Figure 15: Preliminary fire tests and residue yields for (A) unmodified fibers, (B) treated fibers at 10 kGy and (C) at 100 kGy.

4. Conclusion

This study allowed the evaluation of the efficiency of MAPC1 grafting onto flax fibers using a pre-irradiation procedure, for the control of their fire behavior. The radicals concentration in the irradiated fibers increased with the absorbed radiation dose and controlled the grafting reaction. In addition, the effect of grafting parameters such as the absorbed dose, the FR concentration during polymerization reaction, the reaction time and temperature were tuned as these different parameters have a direct influence on the final content of grafted phosphorus FR. The effectiveness of the pre-irradiation grafting was confirmed by SEM pictures showing the presence of phosphorus with a homogeneously localization in the bulk of the fibers whatever the absorbed dose.

Pre-irradiation grafting of MAPC1 onto flax fibers at low doses of 10 kGy and at room temperature resulted in a low degree of grafting with a value of 0.23 wt%. The highest phosphorus content up to 7 wt% was obtained for a 100 kGy-dose and a FR concentration of 10 wt% at 80 °C for 24 hours. However, a low dose of 10 kGy under the same operating conditions allowed us to reach a significant phosphorus content of 2 wt%. This low dose radiation conditions are less degrading for flax fibers and appear to be more attractive for future applications.

This work also confirms that the thermal stability and flammability of treated flax fibers was mainly controlled by the phosphorus content. Char residue, thermal stability and self-extinguishing are dependent on the phosphorus content. The mechanical properties of such treated fibers will be studied in further

investigations.

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6. References

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