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Radiation-grafting of flame retardants on flax fabrics – A comparison between different flame retardant structures

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A B S T R A C T

Three unsaturated compounds bearing respectively phosphate, aryl bromide and sulfenamide moieties were used as flame retardants (FR) for flax fabrics. Due to the presence of carbon-carbon double bonds, radiation-grafting was considered to covalently bond these FR onto fiber structure. Grafting efficiency and location of FR molecules were investigated by weight measurements and SEM-EDX observations. Flammability and especially self-extinguishment were assessed by thermogravimetric analysis, pyrolysis-combustion flow calorimetry and a non-standardized fire test already used in previous studies. All FRs were able to diffuse into elementary fiber bulk. Nevertheless only the phosphonated monomer (noted FR-P) was significantly grafted onto flax. Self-extinguishment was obtained for fabrics containing at least around 0.5 wt% of phosphorus. On the contrary the FR content of flax fibers after radiation-grafting procedure and washing was negligible for FR-S and FR-Br, evidencing that these molecules have not been grafted upon irradiation. Moreover, the combination of these molecules prevents the radiation-grafting of other molecules which showed good grafting rate when used alone.

Keywords:

Flame retardancy

Radiation-grafting

Flax fibers

1. Introduction

Gamma and e-beam irradiation are well-known methods to modify polymer materials. According to the treatment conditions and the considered system, oxidation, grafting, crosslinking, chain scission or a mix of these phenomena can be promoted. Ferry et al. (2016) have recently reviewed the effects of ionizing radiations on polymers and their applications.

Grafting FRs on textiles via irradiation has been explored for a long time. Bromine and phosphorus-based FRs were radiation-grafted onto poly(ethylene terephthalate) fibers by Liepins et al. (1977, 1978). They succeeded to locate selectively FRs at the surface or into the fiber bulk by changing procedure conditions. In particular a pre-swelling step is needed to allow the diffusion of FR into the fibers. Mey-Marom and Rajbenbach grafted bromostyrene onto polyester fabrics by both mutual radiation grafting and pre-irradiation procedures (Mey-Marom and Rajbenbach, 1983). Radiation-grafting of phosphorus-based copolymer on cotton fabric was also explored by Harris et al. (1979). Pre-irradiation was investigated by Khan (2005) in the case of methyl methacrylate grafting onto jute fibers.

Contrarily to dense synthetic fibers, ligno-cellulosic fibers are highly

porous and pre-swelling in solvent is not required to allow the diffusion of molecules into them. This makes the process easier and more suitable for industrial developments. In a previous work we grafted phosphorus FRs onto flax fibers through mutual radiation-grafting (Sonnier et al., 2015). When FR diffuses into fiber bulk during a 1 min impregnation step at room temperature, high grafting efficiency can be reached even at low dose. For example more than 3 wt% of phosphorus (from 17 wt% of dimethylvinyl phosphonate - MVP) was grafted at only 10 kGy. Such a low dose is desirable while it is well-known that cellulose is highly sensitive to irradiation and depolymerization occurs quickly (Bouchard et al., 2006; Le Moigne et al., 2017).

Radiation grafting is particularly suitable for flax fibers or other natural fibers containing low lignin content. Indeed, Horrocks and Zhang (2001) grafted high content of phosphorus from spirocyclic pentaerythritol di(phosphonyl chloride) in very severe and degrading conditions. For temperature lower than 120 °C, the grafting content was very limited. On the contrary, Dorez et al. chose to modify flax fibers using rather soft conditions (Dorez et al., 2014a). They showed that phosphonic acid from octadecylphosphonic acid was grafted only onto lignin but not onto cellulose.

Phosphorus FRs grafted to flax fibers mainly acted as char

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promoters (Sonnier et al., 2015). Good correlations were found between the phosphorus content, the char content and the self-extinguishment. Other FRs with different modes-of-action may be considered as well. Brominated FRs act as flame inhibitors in gaseous phase. Recent works have shown that other classes of FR can act as flame inhibitor, namely azoalkanes and derivatives (Aubert et al., 2011a, b, 2012; Pawelec et al., 2012, 2015; Tirri et al., 2014), disulfides (Pawelec et al., 2014) and sulfenamides (Tirri et al., 2016). They were found to be effective at very low content (typically 0.5 wt%) especially for polyolefins and polystyrene, alone or in synergy with various FRs (brominated FR, alumina trihydrate). In this article three FRs bearing one or two double bonds C=C were attempted to be grafted on flax fabrics by a mutual radiation-grafting procedure. The different steps of the process were studied in order to take new insights about the best strategies to develop self-extinguishing flax fabrics by radiation-grafting.

2. Experimental

2.1. Materials

Flax fabrics were kindly provided by Hexcel. The weight of fabrics was 200 g/m². The composition of flax fibers is 81 wt% of cellulose, 13 wt% of hemicellulose and 2.7 wt% of lignin in good agreement with literature (Maldas et al., 1989, Pallensen et al., 1996, Khalil et al., 2000, Dorez et al., 2014b). These fabrics were already used in our previous studies.

Studied FR structures are shown in Table 1. Ethylene glycol methacrylate phosphate (FR-P) was supplied by Sigma Aldrich. Pentabromophenyl acrylate (FR-Br) was supplied by ABCR (Germany). N,N-diallyl-S-(benzo[d]thiazol-2-yl)thiohydroxylamine (FR-S) was synthesized according to the procedure described in the literature (Davis et al., 1977). For some additional experiments, dimethylvinyl phosphonate (MVP) supplied by Specific Polymers (France) was also used. Its phosphorus content is 22.8 wt%.

2.2. Fiber grafting procedure

The general procedure for the fabrics impregnation with FR is shown in Fig. 1. In a first step the flax fabric was dipped one minute into a solution of FR monomer and tetrahydrofuran (THF). The FR concentration was 1, 5 or 10 wt/wt%. After impregnation the fabric was placed under a laboratory extractor hood to remove the solvent (THF). Fibers were irradiated in air at room temperature using an electron beam accelerator (energy 9.8 MeV, power 27 kW) by Ionisos SA (Chaumesnil, France). Doses were chosen in the range 10–50 kGy. After irradiation the washing of the fabric with THF allowed removing ungrafted molecules.

3. Characterizations

3.1. Grafting content

FR content in fabrics was assessed firstly by weighing. Indeed

samples were weighed before and after impregnation with the FR but also after the radiation-grafting and after washing with THF.

An Oxford XMET 5100 X-ray fluorescence analyzer was also used to determine more precisely the phosphorus elemental analysis in treated flax fabrics. Samples were fixed on a flat polymer holder. This holder was chosen because it does not contain any phosphorus traces and to reduce instrumental errors. This analysis was achieved under atmospheric pressure, without any preparation. The following settings were used as default: 13 kV and 45 μ A. Each spectrum was collected with a fixed measuring time (60 s). As the intensity of the phosphorus K α peak is proportional to its concentration, the data were collected and converted by a simple calculation to determine the weight percentage of phosphorus. This instrument was calibrated from measurements carried out using samples of known phosphorus concentration and prepared in our previous work (measured by ICP-AES - inductively coupled plasma atomic emission spectroscopy). A calibration curve was drawn with a high correlation coefficient. Peak intensity was converted into phosphorus weight percentage using this calibration curve. Phosphorus content was also measured from ICP-AES for two fabrics prepared in the present study. Measurements were carried out by SGS Multilab.

3.2. Scanning electron microscopy (SEM) coupled EDX analyses

The micrographs of the fibers were obtained using an environmental scanning electron microscope (FEI Quanta 200). For this study, the fibers were cut while avoiding damaging them by stretching or crushing. Then they were deposited on an adhesive wafer so that the facies are at the edge of the wafer. They were metallized with carbon in high vacuum sputtering metallizer Bal-Tec CED 030 Balzers in order to ensure their stability during the analysis. The so prepared fibers were analyzed using a vertical sample holder and the micrographs were obtained under high vacuum at a voltage of 7 kV, with a spot size lower than 1 μ m and a working distance of 10 mm. The environmental SEM was equipped with an Oxford energy-dispersive X-ray spectroscopy (EDX) sensor which enables to carry out elemental imaging on fibers.

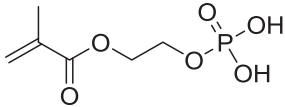
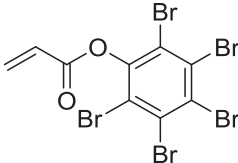
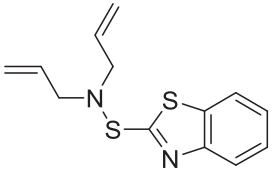
3.3. Thermogravimetric analysis

Thermal stability of samples was determined using TGA (Pyris 1, Perkin-Elmer). Sample weight was approximately 5 mg. Experiments were performed between 30 and 750 °C at 10 °C/min under nitrogen (20 mL/min).

3.4. Pyrolysis combustion flow calorimetry

The pyrolysis combustion flow calorimetry (PCFC) is used to assess the flammability of samples at microscale (2–3 mg). This device was developed by Lyon and Walters (Lyon and Walters, 2004). The sample was first heated from 80 to 750 °C at 1 °C/s in a pyrolyzer under nitrogen flow (anaerobic pyrolysis – method A according to the standard ASTM D7309) and the degradation products were sent to a combustor where they mixed with oxygen in excess at 900 °C. In such conditions, all gases were fully oxidized. Heat release rate (HRR) was then calculated by

Table 1
Chemical structure of the three studied FR.

		
FR-P P content 14.7 wt%	FR-Br Br content 73.6 wt%	FR-S S content 24.4 wt%

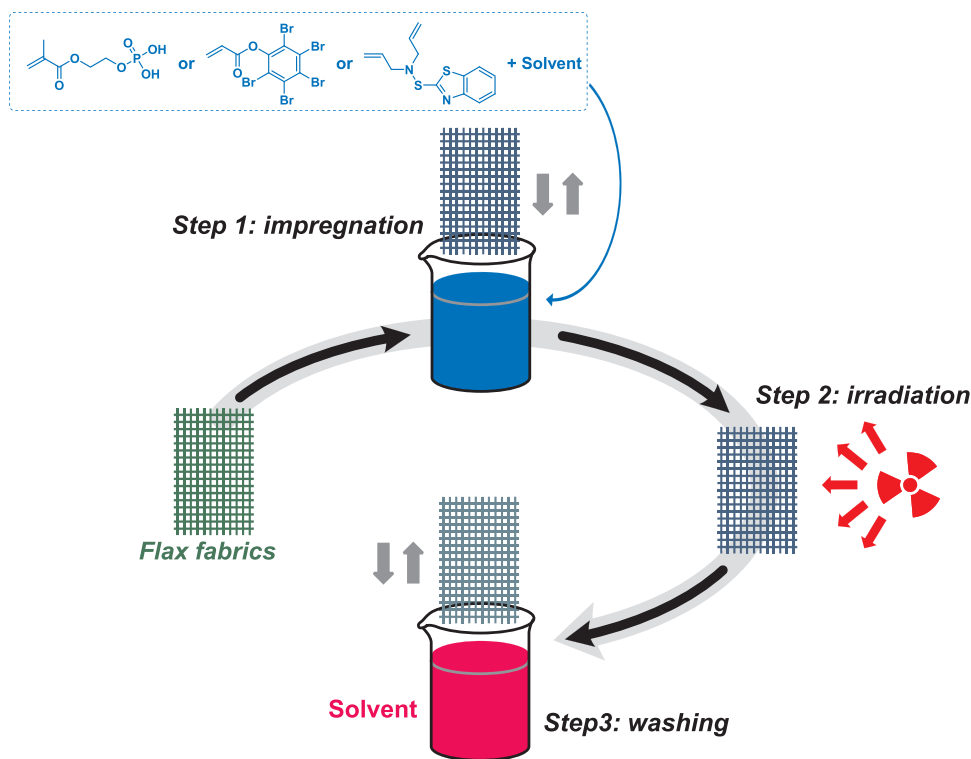


Fig. 1. General procedure for flax fabrics modification.

oxygen depletion according to Huggett's relation (1 kg of consumed oxygen corresponds to 13.1 MJ of released energy) (Huggett, 1980).

3.5. 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 0.5 g) are pinched between two glass plates and maintained vertically. A lighter is used to ignite the top of fabrics. This device allows assessing if the fabric is self-extinguishing. The residue is also weighed after complete burning. The weight of the fabric pinched between plates is subtracted from the residue weight. For self-extinguishing fabric, complete burning is reached by multiple flame applications. As already shown in our previous work, this test is reproducible and allows assessing the self-extinguishment and the charring of the fabrics. This information is sufficient to guide our research and development efforts.

4. Results and discussion

4.1. Measurement of FR contents

The FR treatment process is based on three successive steps, namely impregnation, radiation-grafting and washing. Its success 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 (i.e. few molecules are removed after washing). To control these phenomena, samples were weighed systematically after each step.

Fibers weight gain after impregnation (and solvent removal) depends strongly on the FR concentration in solution (Fig. 2), from a gain of 2.7 ± 0.3 wt% for a 1 wt% FR solution to a gain of 18 ± 2 wt% for 10 wt% FR solution. It is noteworthy that there are few differences between the three FR molecules. The weight gain seems to be slightly higher for FR-S and slightly lower for FR-P. This may be assigned to a lower diffusion of FR-P into fiber bulk as revealed by SEM pictures (see below). These results confirm that the process is mainly controlled by FR concentration in solution as already noted in our previous work (Sonnier et al., 2015).

After impregnation and solvent removal, the samples are kept at

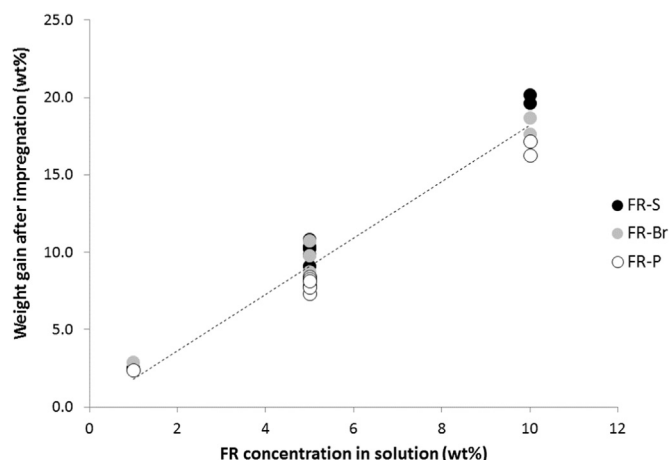


Fig. 2. Weight gain after impregnation (wt%) versus FR concentration in solution (wt%).

room temperature and sent to Ionisos company for radiation-grafting. The period between impregnation and radiation typically ranges from two to three weeks. Volatilization of small molecules can occur. Figs. 3 and 4 show the fraction of non-volatilized FR (i.e. remaining after irradiation) according to the following equation.

$$\text{Fraction of non-volatilized FR} = \frac{\text{Weight gain after irradiation}}{\text{Weight gain after impregnation}}$$

Volatilization is null for FR-Br whichever the FR concentration in solution or the absorbed dose (fractions slightly higher than 1 are due to measurement uncertainties, especially because fibers are sensitive to relative humidity). Volatilization of FR-P is limited. Typically the fraction of non-volatilized FR-P remaining in the fibers after the waiting period and irradiation is 0.8–0.9. This fraction is slightly lower at low FR concentration (0.7). In the case of FR-S, the volatilization is more significant and increases when the FR concentration in solution decreases. The fraction of non-volatilized FR-S is 0.8 for 10 wt% of FR-S in solution but only 0.43 for 1 wt% of FR-S in solution. Dose does not

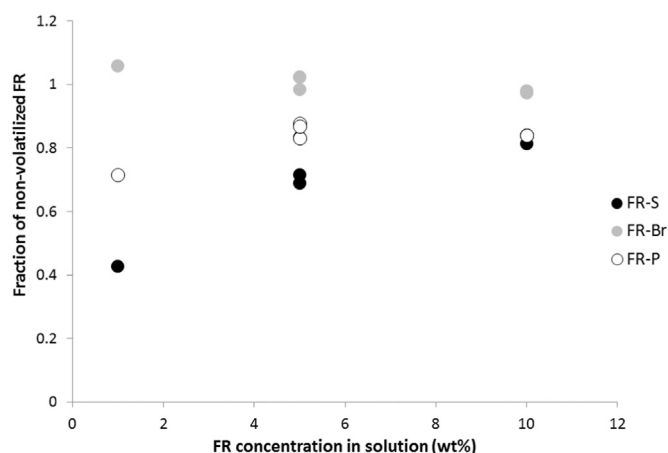


Fig. 3. Fraction of non-volatilized FR versus FR concentration in solution (wt%) – Absorbed dose is fixed to 50 kGy.

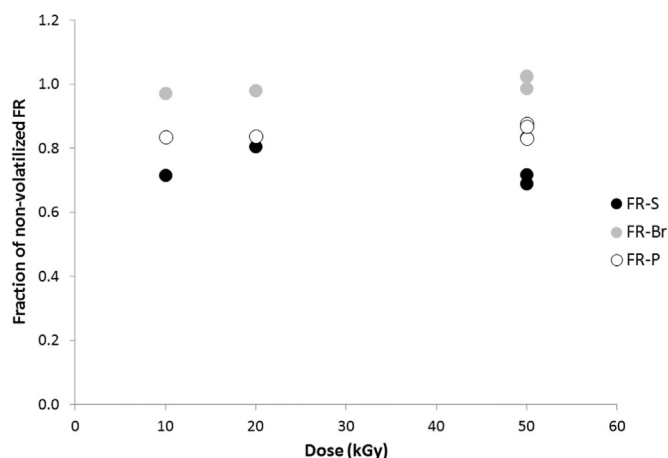


Fig. 4. Fraction of non-volatilized FR versus absorbed dose (kGy) – FR concentration in solution is fixed to 5 wt%.

influence the rate of volatilization of FR-P and FR-S. Note also that the molar mass of the FR is not the main parameter influencing the volatilization. Indeed, FR-S has a higher molar mass but also a higher rate of volatilization than FR-P.

Grafting efficiency is defined as the ratio between the weight gain after washing and the weight gain after irradiation. It must be mentioned that the molecules which are not removed by washing are not necessarily grafted to flax fibers. Indeed, FR-P and FR-Br may homopolymerize during the irradiation step and the obtained polymer chains can be trapped into the fibers, in such a way that washing is not able to remove them. Nevertheless, in the case of FR-S, homopolymerization will not occur as demonstrated in the literature (Masterova et al., 1976; Volodina et al., 1970) limiting therefore the presence of FR-S after washing to only the grafted molecules. From a practical point of view, the polymeric FRs remain in the fibers and have a high thermal stability (they are not volatilized at low temperature during heating). Then the trapping (even without grafting) is not an issue for composite applications requiring processing steps at high temperature.

Grafting efficiency is significant for FR-P ranging between 40 and 50 wt% whatever the FR concentration in solution and the absorbed dose. Nevertheless these values are lower than those obtained with MVP in our previous work (from 60 to 95 wt%). Absorbed dose slightly increases the grafting efficiency as already observed. When more radicals are created, the probability to graft FR-P to flax or to trap polymer chains in the fiber structure is enhanced. Nevertheless the change is quite limited. This result confirms that the dose is not the main process parameter monitoring the final weight gain in the studied

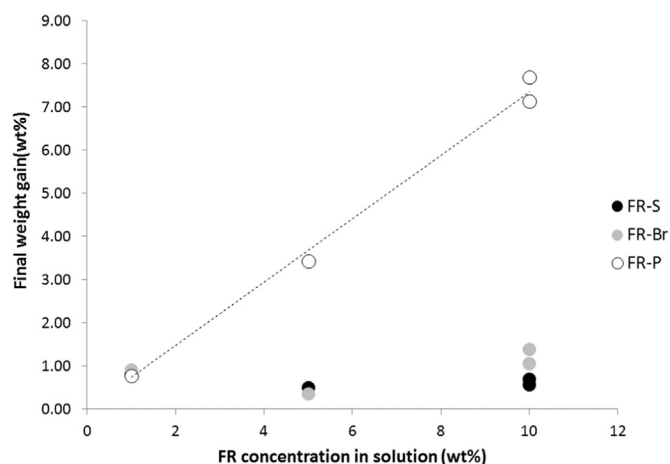


Fig. 5. Final weight gain (wt%) versus FR concentration in solution – Absorbed dose 50 kGy.

dose range. Nevertheless, dose dependency may be observed for doses lower than 10 kGy and saturation may occur at this dose.

Grafting efficiency is very low for both FR-S and FR-Br. SEM observations show that FR-Br and FR-S are homogeneously present into the fiber bulk after impregnation. Then the low grafting efficiency may be assigned to the low reactivity of these molecules upon irradiation. Indeed, brominated FRs are efficient radical scavengers and this is why they are used as FRs (Noto et al., 1996). In the case of FR-S, its impossibility to form homopolymer (as reported above), the limited reactivity of the allyl group compared to the methacrylic group towards grafting and its antioxidant activity could explain these results.

Final weight gain is the main value to be considered in order to develop self-extinguishing fabrics (Figs. 5 and 6). Even if the weight gain after impregnation is similar for the three molecules, volatilization and above all grafting efficiency lead to great differences in terms of final weight gain. Final weight gain is very low for FR-S and FR-Br (< 1.3 wt%). On the contrary, the final weight gain reaches 7.7 wt% for FR-P. This value increases linearly with the FR concentration in solution (i.e. also the weight gain after impregnation). Once again this result confirms our previous findings.

Phosphorus content was calculated from X-ray fluorescence analysis, after calibrating with elemental analysis by ICP-AES. For two fabrics, phosphorus content was also directly measured by ICP-AES. Fig. S1 compares the phosphorus contents calculated from ICP-AES, X-ray fluorescence and weight measurements (considering that P content in FR-P is 14.7 wt%) for fabrics after radiation-grafting (before or after

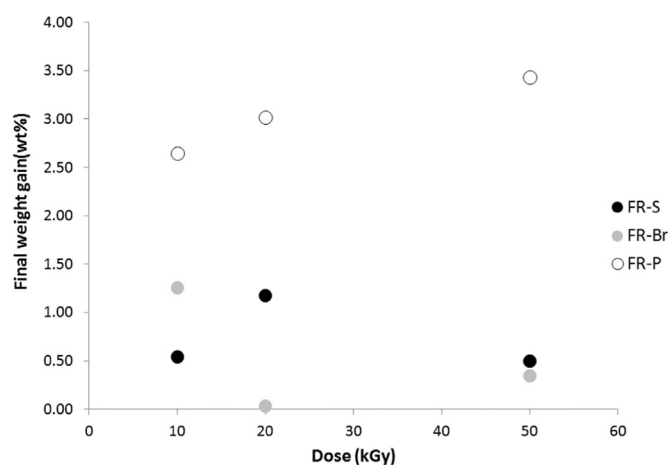


Fig. 6. Final weight gain (wt%) versus absorbed dose (kGy) – FR concentration in solution 5 wt%.

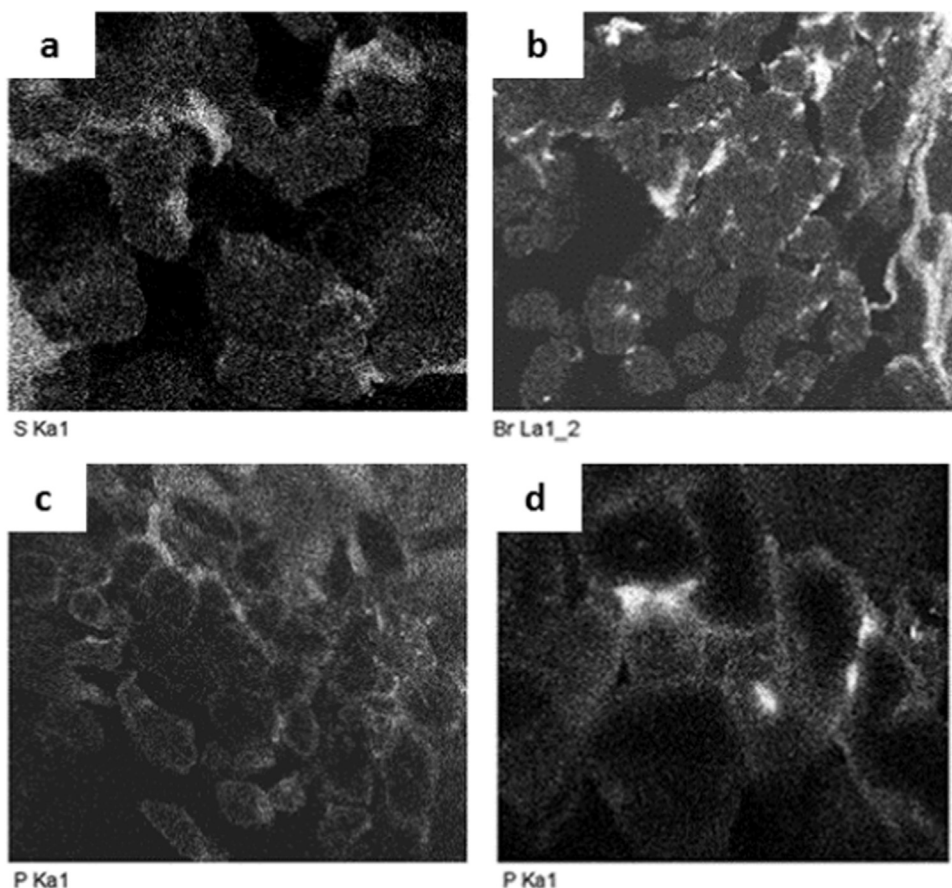


Fig. 7. S (a), Br (b) and P (c) mapping for flax modified respectively with FR-S, FR-Br and FR-P after impregnation (FR concentration in solution 5 wt%) – (d) P mapping for flax modified with FR-P after the whole process (FR concentration in solution 5 wt%, absorbed dose 50 kGy).

washing). Correlation between these calculations is rather correct for low to moderate phosphorus content but it appears that weight measurements overestimate the phosphorus content, especially at high content (> 1 wt%). The presence of FR-P may modify the water uptake of the fibers which limits the accuracy of the weight measurements to assess the grafting efficiency. Note that critical phosphorus content for self-extinguishing behavior is around 0.5–0.8 wt% as discussed in the following. Therefore, weight measurements seem to be suitable to assess the phosphorus content in this range.

4.2. Location of FR into elementary fiber section

The relatively high weight gain after impregnation suggests that all FRs diffuse easily into fiber bulk. SEM-EDX observations confirm this assumption (Fig. 7). FR-S and FR-Br are well distributed into the whole section of the fibers (see respectively Fig. 7a and b). In the case of FR-P, it seems that the molecule is located preferentially near the surface (Fig. 7c). The gradient of concentration from the surface to the core can be assigned to a slightly higher difficulty to diffuse through the fiber section. This would explain why the weight gain after impregnation is slightly lower for FR-P.

After irradiation and washing, FR-Br and FR-S are almost completely removed from fibers in good agreement with weight measurements. FR-P is still present (Fig. 7d). The distribution is still quite heterogeneous. The presence of FR-P appears more significant into some fibers than other ones. The concentration is still higher at the surface. Moreover high concentration spots are detected into some hollows and especially into the fiber lumens. These hollows may trap FR-P molecules.

4.3. Flammability

Flammability was assessed using PCFC. Fig. 8 shows the heat release rate curve for unmodified fabric and some fabrics modified with FR (FR

concentration 5 wt% in solution, dose 50 kGy).

Fig. 8a shows the heat release rate for fabrics modified with FR-Br. The presence of FR-Br leads to a decrease in thermal stability. However this decrease is moderate in comparison to FR-P: only 15–25 °C (from 367 °C to 340–350 °C). The pHRR is not reduced and even significantly higher after impregnation. This may be due to a catalytic degradation of flax by FR-Br. THR remains constant (around 8–10 kJ/g) and no additional char is formed. After washing, few FR-Br molecules are still present (weight gain less than 0.5 wt%). PHRR as well as temperature at pHRR get closer to the values of unmodified fabrics.

Heat release rate curves for fabrics modified with FR-S are shown in Fig. 8b. As for FR-Br, the temperature at pHRR slightly decreases after impregnation (by 10–15 °C). THR remains constant and pHRR slightly decreases. After washing (weight gain is less than 0.5 wt%), temperature at pHRR does not change anymore. PHRR is similar to that of unmodified fabric. On the whole, no obvious decrease in flammability is observed in the presence of FR-Br and FR-S. After washing, the curves get closer to that of unmodified fabric but thermal stability remains slightly lower. These results seem to indicate that radical generators need to be optimized for flax fabrics in order to show higher FR effect in this material.

On the contrary, the presence of FR-P leads to a large decrease in peak of heat release rate (pHRR) and total heat release (THR) due to char promotion (Fig. 8c). Thermal stability is also significantly affected: pHRR occurs at 367 °C for unmodified fabric and only 260 °C for modified fabrics. Radiation-grafting does not change appreciably the flammability in comparison to only impregnation despite a lower weight gain due to partial volatilization and removal of unreacted molecules by washing (3.4 wt% versus 8.2 wt%). This may be indicative of a higher efficiency of FR-P when grafted.

All these changes are in close agreement with those previously obtained about flax fibers modified with phosphorus FRs (Sonnier et al., 2015, Dorez et al., 2014c). The decrease in thermal stability is usual when phosphorus flame retardants are added into polymers including

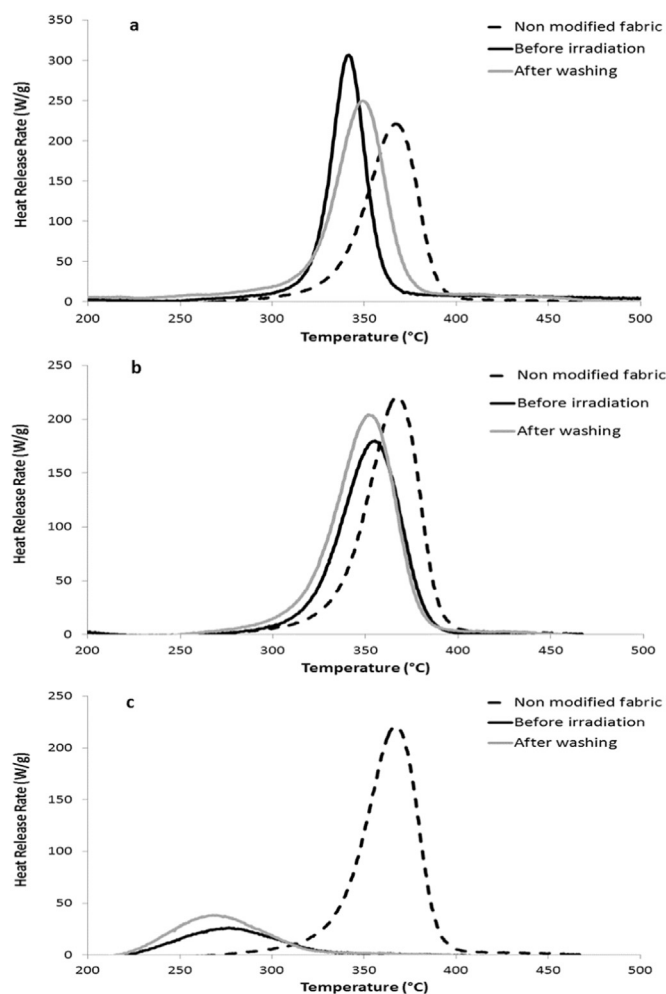


Fig. 8. Heat release rate curves for fabrics unmodified and modified with FR-Br (a), FR-S (b) and FR-P (c) (FR concentration in solution 5 wt%, absorbed dose 50 kGy).

lignocellulosic materials. Indeed, phosphorus flame retardants decompose into phosphoric acids and dehydrate cellulose promoting its charring (Chapple and Anandjiwala, 2010).

Fig. 9 and S2 show the change in pHRR and temperature at pHRR for all fabrics modified with FR-P but also with other phosphorus FRs (MVP and MAPC1 - Dimethyl(methacryloxy)methyl phosphonate) studied in our previous work. Phosphorus content with FR-P does not reach values as high as with MVP (Sonnier et al., 2015). At comparable phosphorus contents (between 0.5 and 1.5 wt%) it seems that changes are slightly more significant with FR-P: pHRR is lower (around 50 W/g versus 80 W/g for MVP) and temperature at pHRR is 20 °C lower.

4.4. Assessment of self-extinguishment

As in our previous work, self-extinguishment was assessed by a non-standardized fire test (see Fig. S3). Fabrics modified with FR-P are self-extinguishing except that with the lowest phosphorus content. The flame vanishes at the same moment when the burner is removed. The flame out even seems to be faster than with MVP (see previous work). Results of fire test are plotted in Fig. 10 together with those from previous works (Sonnier et al., 2015). Even if this test does not allow an accurate discrimination between FR from the efficiency point of view, it appears that char content is higher for FR-P and self-extinguishment is obtained at lower P content: 0.45 wt% of P is enough for FR-P to ensure self-extinguishment while 0.5 wt% of MVP were found too low for this purpose.

Radiation-grafting is a necessary step to bond covalently FR onto flax fibers structure and to avoid its release at low temperature. But it is

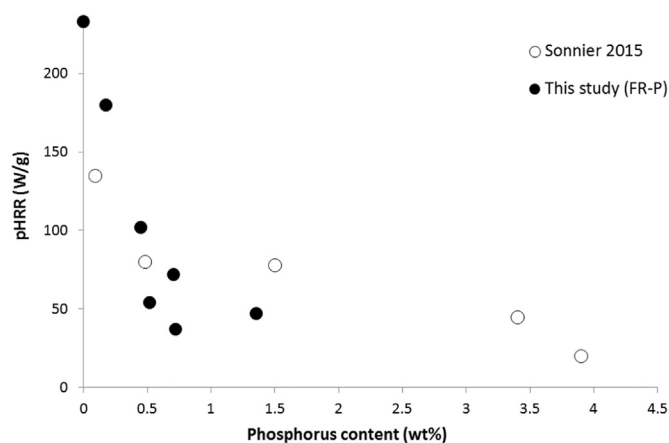


Fig. 9. Change in pHRR versus phosphorus content for fabrics modified with phosphonated monomers (FR-P for this study and MVP for previous work).

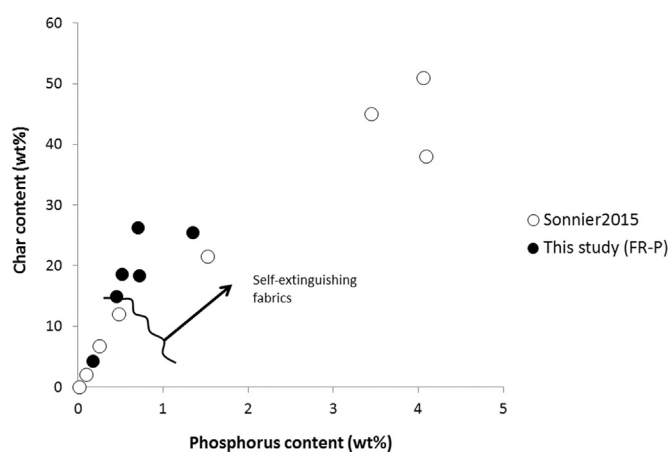


Fig. 10. Char content and self-extinguishment from fire test versus phosphorus content for fabrics prepared with various phosphorus-based FRs.

also of interest to assess if grafting has an influence on the flame retardancy efficiency of FR-P. Some fabrics were impregnated with various amounts of FR-P without further grafting. One fabric was irradiated but not washed. Fire performances are plotted in Fig. 11 versus the weight gain. Only the non-irradiated fabric with the highest weight gain is self-extinguishing. It seems that for similar weight gain (and then similar phosphorus content), radiation-grafted fabrics exhibit higher char contents and are more easily self-extinguishing. These first

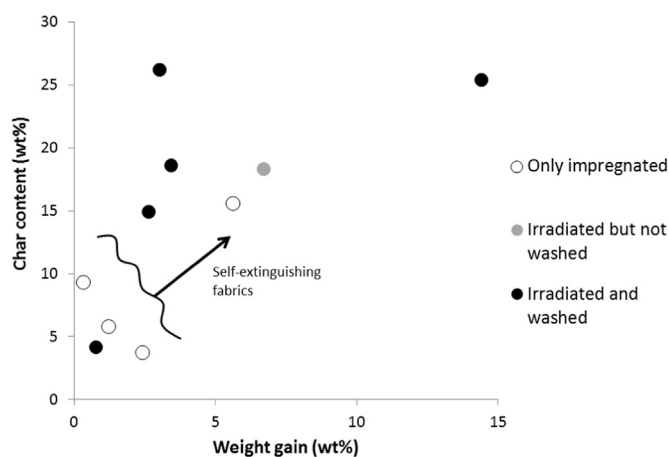


Fig. 11. Char content and self-extinguishment from fire test versus weight gain for fabrics prepared with various phosphorus-based FRs and different procedures.

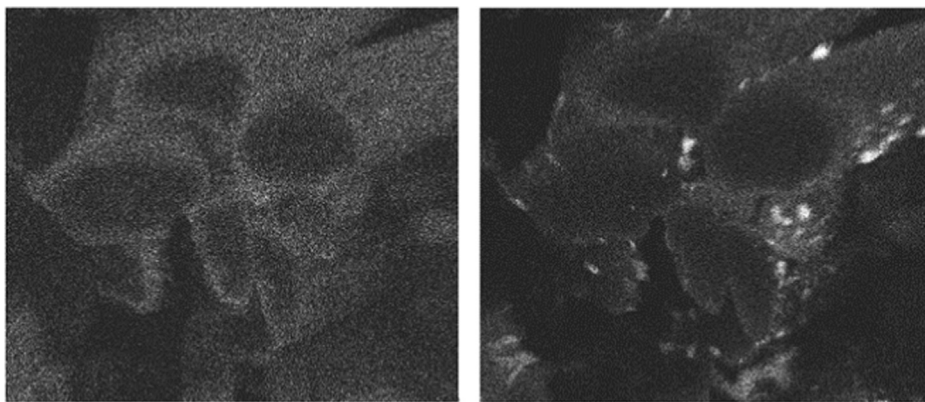


Fig. 12. P mapping (left) and Br mapping (right) for flax fabrics after impregnation with a THF solution containing 5 wt% of FR-P and 5 wt% of FR-Br, absorbed dose 50 kGy and purification by THF washing.

indications can be explained by the fact that a release of FR-P at too low temperature does not promote efficiently the charring of flax fibers. This confirms previous indications from PCFC results: similar pHRR is obtained with lower phosphorus after radiation-grafting and washing. Further investigations based on more discriminant tests are needed to confirm this assumption.

Fabrics modified with FR-Br are not self-extinguishing due to the low content of FR after washing. When the fabric is only impregnated with FR-Br (5 wt% of FR-Br in solution, 8.2 wt% of FR-Br in flax), self-extinguishment is still not observed. However after irradiation (50 kGy), the same fabric (with the same amount of FR-Br, keep in mind that this FR does not volatilize) becomes self-extinguishing. The flame does not vanish instantaneously but few seconds after the burner removal. It means that the efficiency may be improved to a certain extent by irradiation despite FR-Br units do not graft onto flax fibers. The reason for this result is unclear and is not expected from analysis at microscale. Indeed, TGA were carried out before and after irradiation (Fig. S4). No change in thermal degradation was observed.

None of the fabrics modified with FR-S is self-extinguishing. Similar burning behavior was observed with irradiated fabrics containing higher (non-washed) or lower (washed) FR content or with non-irradiated fabric at 9.8 wt% FR loading. These results indicate that the current FR-S structure is not the most appropriate for flax fabrics and would require tailoring to improve its activity. In fact, it has been shown, in previous work, that one specific sulfenamide can be very effective in a specific substrate but much less in another one. FR-S exhibits multifunctionality such as antioxidant activity, cross-linking ability and moderate FR activity in polyolefins but is not fine-tuned for application in cellulosic materials.

4.5. Combination of FR: preliminary results

While phosphorus-based FRs are easily grafted into fibers, FR-Br and FR-S are not grafted and are removed during washing. Nevertheless, the high reactivity of some phosphorus-based FRs as MVP upon irradiation may allow FR-Br or FR-S to be grafted using a copolymerization strategy. To assess this assumption, flax fabrics were impregnated with a solution containing 5 wt% of MVP and 5 wt% of FR-S or FR-Br before to be irradiated at 50 kGy. Unfortunately, in the presence of FR-S, no grafting occurs even for MVP and the fabric burns promptly. The radical scavenging property of FR-S could explain this behavior.

In the presence of FR-Br, both phosphorus and bromine are observed by SEM-EDX after washing, mainly at the fibers surface (Fig. 12). Nevertheless, the weight gain after washing is low: 2.04 wt%. The phosphorus content is very low: 0.13 wt% according to X-ray fluorescence analysis, corresponding to 0.57 wt% of MVP. If we consider the amount of MVP, it means that the gain weight in FR-Br is 1.47 wt%. This content is slightly higher than those measured for fabrics modified with FR-Br used alone. But it remains too low to reach self-

extinguishment (char content in fire test was only 7 wt% while self-extinguishment is usually observed for a char content around 15 wt% - see Fig. 10). These results highlight the detrimental role of FR-S and FR-Br on grafting.

5. Conclusion

This article highlights that the success of mutual radiation-grafting of FR on flax fibers depends on a couple of parameters. FR-P is the third phosphorus-based FR to be tested for radiation-grafting on flax. All these phosphorus monomers are significantly grafted or trapped after homopolymerization into fiber bulk. The diffusion into flax during impregnation is the most important step to control the final phosphorus content through the FR concentration in solution.

Grafting is negligible for the bromine FR and the sulfenamide FR, probably because these molecules are efficient radical scavengers. In other words, radiation grafting is not suitable for FR molecules acting as radical scavenging (flame inhibitor) in the conditions applied in this work. To assess correctly the efficiency of these molecules as FRs, other strategies should be considered. Nevertheless, in the case of FR-Br, radiation process seems to improve its flame retardancy to a certain extent. Further investigations are needed to confirm this point. Another possibility is that the carbon-carbon double bond of these molecules is not reactive enough upon irradiation or cannot homopolymerize like in the case of FR-S regardless of their radical scavenging behavior.

This work also confirms that high charring content is closely related to the phosphorus content in fabrics modified with phosphorus-based FRs. These FRs monitor the flax degradation which occurs earlier and promote the charring of flax. The FR-P studied in this article seems to be slightly more efficient than other FRs previously studied. Indeed, self-extinguishment is obtained for phosphorus content around 0.5 wt%.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.radphyschem.2017.10.013>.

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