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Chemical treatments of flax fibers – Control of the diffusion of molecules into the fiber structure

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ABSTRACT

This study concerns the control of the diffusion of molecules and macromolecules in the structure of flax fibers during the impregnation step of a radiation grafting procedure. In this work we essentially focused on the impact of the conditions used during the impregnation of flax fabrics on localization of the treatment agent in the fibers structure. In a first step fabrics were impregnated by dipping them into a solution containing different chemical monomers, polymers or copolymers combined with various solvents. After solvent elimination, fibers were characterized by SEM/EDX to evaluate the presence of the treatment agents in their structure. Influences of treatment agent and solvent combination and duration of the impregnation step were evaluated. The re-gioselective localization at the surface or the presence in the whole fiber can be obtained through a suitable choice of the treatment agent and the solvent. The duration of the impregnation process can also modify this localization when the affinity between the treatment agent and the solvent is low. Two new strategies of double functionalization were successfully developed. The first one is based on the repetition of the irradiation sequence (impregnation, irradiation, washing) on the same sample but with change of the treatment agent for the second cycle. The second strategy is based on a single impregnation step with a regioselective localization of the treatment agents due to their differences of affinity with solvent used.

Keywords:

Flax fibers

Chemical treatment

Regioselective modification

Radiation grafting

1. Introduction

Nowadays, the use of plant fibers for composite applications is a real alternative to synthetic fibers (Alkbir et al., 2016; Bharath and Basavarajappa, 2016; Faruk et al., 2012; Fuqua et al., 2012; Pickering et al., 2016; Thakur et al., 2014). These natural reinforcements found many applications in composites materials due to their numerous advantages (Biagiotti et al., 2004; Fuqua et al., 2012; Puglia et al., 2005; Ramamoorthy et al., 2015; Saheb and Jog, 1999): renewability, biodegradability, low cost, low density, low abrasiveness (in comparison to fiberglass) and good mechanical properties. Nevertheless, weaknesses still limit their application in some industrial fields such as low compatibility with some polymer matrices like polyolefins, thermal sensitivity at the temperature of compounding process and flammability (Ahmad et al., 2015; Azwa et al., 2013; Chapple and Anandjiwala, 2010; Prabhakar et al., 2015; Saheb and Jog, 1999). Chemical modification of plant fibers is one of the more interesting solutions to improve the fiber-matrix interface and modify the fiber properties. This modification can be performed by various treatments (Ali et al., 2016;

Bledzki et al., 1996; George et al., 2001; Hassan and Wagner, 2016; Le Moigne et al., 2018; Saha et al., 2016): impregnation, chemical coupling, enzymatic, corona, plasma, UV irradiation, gamma or electron beam irradiation.

In the literature, several characterization methods have been used to prove the chemical modifications of plant fibers (Le Moigne et al., 2018). The most commonly methods used are Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) but authors also used gravimetric method, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), SEM coupled with energy dispersive X-ray analysis (EDX), elemental analysis by combustion analysis (CHNS elemental analysis) or inductively coupled plasma atoms emission spectroscopy (ICP-AES), Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), Pyrolysis combustion flow calorimeter (PCFC), FT-RAMAN, and solid-state nuclear magnetic resonance (NMR).

Generally authors use these methods to prove the chemical modification of plant fibers and some of them evaluate also the grafting rate. But the location of the chemical modification in the fibers structure is

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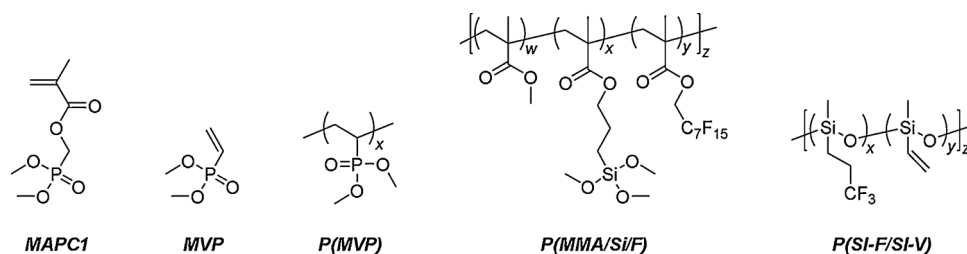


Fig. 1. Chemical structure of MAPC1, MVP, P(MVP), P(MMA/Si/F) and P(SI-F/SI-V).

usually not considered. In the literature only few studies deal with the location of the grafting agent in the fiber. Mangiante et al. (Mangiante et al., 2013) studied the alkylation of cellulose fibers and used Raman and fluorescence confocal microscopies to characterize the presence of the functionalizing agent all over the cross section of the fibers. With the same objective, we described in several previous studies the use of SEM-EDX to characterize the chemical modification of flax fibers (Dorez et al., 2014; Hajj et al., 2018; Sonnier et al., 2015; Teixeira et al., 2018). The location of different grafting agents was observed by phosphorus, bromine or sulfur mapping using EDX analysis. This technique allowed the observation of the grafting agent diffusion in the flax fibers structure. Indeed we proved the chemical modification either only at the surface, or at the surface and in the bulk of the elementary fibers depending on the chemical structure of the grafting agent used. Flax as the wide variety of plant fibers has a complex chemical composition and structure, with complex assemblies of several components. Cellulose and hemicellulose are the main components of cell walls of plants. These compounds are associated in a complex manner with each other and with small amounts of lignin, proteins, extractives (e.g. fatty acids and alcohols, sterols, ferulic acid esters, waxes, aromatic compounds...), and inorganic components that include minerals and metals (e.g. silica, calcium, potassium, zinc, iron, lead...) (Goudenhooff et al., 2018, 2017; Müssig, 2010; Yan et al., 2014). As the chemical composition of the flax fibers is not homogeneous, we assume that the diffusion of molecules or macromolecules through their structure can be different according to their affinity with the chemical composition of the different components. This phenomenon of chromatography separation where the flax fiber is the stationary phase should be controlled by the modification of temperature, time of impregnation and solvent nature. This separation should involve during the fibers impregnation step that we previously described for the procedure of flax modification with flame retardant monomers using a radiation grafting (Hajj et al., 2018; Sonnier et al., 2015; Teixeira et al., 2018). During this step flax fabrics are dipped for one minute in a monomer/solvent mixture to allow the monomer to penetrate in the fibers. After solvent elimination monomer is polymerized or grafted using a radiation process. In this study, the relationships between the impregnation conditions of flax fabrics with molecules and the location of these compounds in the fiber structure were investigated. The influences of the nature and the size of the treatment agent, the solvent, and the impregnation duration were studied. Based on the results exposed in the first part of the article, two different methods were developed to prepare regioselective multi-functionalized flax fabrics. This work focuses only on the influence of fibers treatment conditions on the location of the treatment agents in their structure. The impact of these treatments on flax fibers properties is not discussed in this article.

2. Material and methods

2.1. Materials

Flax fabrics with area density 200 g/m², twill 2 × 2, yarn low twist (68 tex i.e. 68 g/km), were kindly provided by Hexcel (France). 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 and was determined using an extractive method (Acerá Fernández et al., 2016). Dimethyl(methacryloxy)methyl phosphonate (MAPC1, Specific Polymer), dimethylvinyl phosphonate (MVP, ABCR), methylmethacrylate (MMA, Sigma Aldrich), 3-(trimethoxysilyl)propyl methacrylate (MPS, ABCR), 1H,1H-Perfluorooctyl methacrylate (C₇F₁₅CH₂-MA, ABCR), 2,2'-azobis(2-methylpropionitrile) (AIBN, Sigma Aldrich), (98–99% methyl-3,3,3-trifluoropropylsiloxy)-(1–2% methylvinylsiloxy) copolymer (P(SI-F/SI-V), ABCR), acetonitrile (Merck), tetrahydrofuran (THF, Fisher Scientific), ethanol (Fisher Scientific) and methanol (Fisher Scientific) were used as received without any purification. The chemical structures of MAPC1, MVP, P(MVP), P(MMA/Si/F) and P(SI-F/SI-V) used for the flax fabrics treatment are given in Fig. 1. For ease of reading, the various abbreviations used in the text for the different chemicals are listed in Table 1.

2.2. Synthesis of fiber-treating agents

The procedures to synthesize the polymers P(MVP) and P(MMA/Si/F) are represented in Fig. 2.

2.2.1. Synthesis of the homopolymer P(MVP)

The synthesis consisted in a radical polymerization of MVP in acetonitrile under argon atmosphere. Into a 100 mL flask fitted with a condenser 10 g (7.3 × 10⁻² mol) of MVP, 0.12 g (7.3 × 10⁻⁴ mol) of AIBN and 10 g of acetonitrile were introduced. Argon was bubbled through the mixture for 15 min. The mixture was then stirred and heated at 80 °C for 15 h. After reaction the polymer was purified by precipitation in diethyl ether. Fig. 3 shows the ¹H NMR spectrum in deuterated chloroform of the product obtained.

2.2.2. Synthesis of the copolymer P(MMA/Si/F)

The radical copolymerization of MMA, MPS and C₇F₁₅CH₂MA was carried out under argon atmosphere. Into a 100 mL flask fitted with a condenser 10 g (0.1 mol) of MMA, 3.1 g (1.2 × 10⁻² mol) of MPS, 5.8 g (1.2 × 10⁻² mol) of C₇F₁₅CH₂MA, 0.21 g (1.3 × 10⁻³ mol) of AIBN and 16 g of acetonitrile were introduced. Argon was bubbled through the mixture for 15 min. The mixture was then stirred and heated at 80 °C for

Table 1

list of the abbreviations used for the monomers, polymers and solvents used in this study for the flax treatments.

Notation	Chemical product
THF	Tetrahydrofuran
MMA	Methylmethacrylate
MPS	3-(Trimethoxysilyl)propyl methacrylate
MAPC1	Dimethyl(methacryloxy)methyl phosphonate
MVP	Dimethylvinyl phosphonate
C ₇ F ₁₅ CH ₂ MA	1H,1H-Perfluorooctyl methacrylate
P(MVP)	Poly(dimethylvinyl phosphonate)
P(MMA/Si/F)	Poly(methylmethacrylate-co-3-(trimethoxysilyl)propyl methacrylate-co-1H,1H-perfluorooctyl methacrylate)
P(SI-F/SI-V)	Poly(methyl-3,3,3-trifluoropropylsiloxy-co-methylvinylsiloxy)

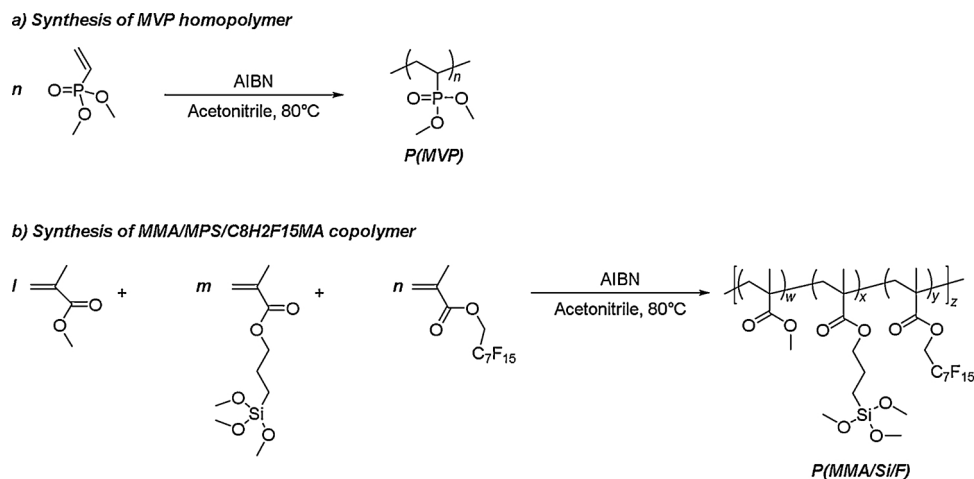


Fig. 2. Synthesis of a) the homopolymer P(MVP) and b) copolymer P(MMA/Si/F).

15 h. After reaction the polymer was purified by precipitation in methanol. Fig. 3 shows the ^1H NMR spectrum in deuterated DMSO of the product obtained.

2.3. Samples preparation

2.3.1. General procedure

Generally the irradiation grafting procedure comprises three steps. The first one is an impregnation step which makes it possible to introduce the grafting agent. The second one is an irradiation step to fix the grafting agent on the structure of the flax. The last one is a washing step to eliminate unreacted or non-fixed molecules to the structure of flax. However, in this study we are mainly interested in the impregnation stage. The flax fabrics were dipped into a solution containing the molecule(s) or macromolecule(s). A large set of molecules, solvents and impregnation durations were investigated. After this first step, the

fabrics were placed at room temperature under a laboratory extractor hood to remove the solvent. The drying time of the treated flax fabrics depends on the solvent used. For example, the times measured are respectively 5, 6, 15 and 55 min for THF, acetone, ethanol and water. When needed, fabrics were irradiated at 50 kGy in air at room temperature using an electron beam accelerator (energy 9.8 MeV) by Ionisos SA (Chaumesnil, France). After irradiation the washing of the fabric with THF or ethanol allowed removing ungrafted molecules. Ethanol was chosen because it has better affinity with poly(MAPC1) and poly(MVP) than THF.

Samples were weighted before and after impregnation with the monomers and polymers but also after the irradiation step before and after washing steps in order to evaluate the grafting efficiency. All prepared fabrics are listed in Table 2.

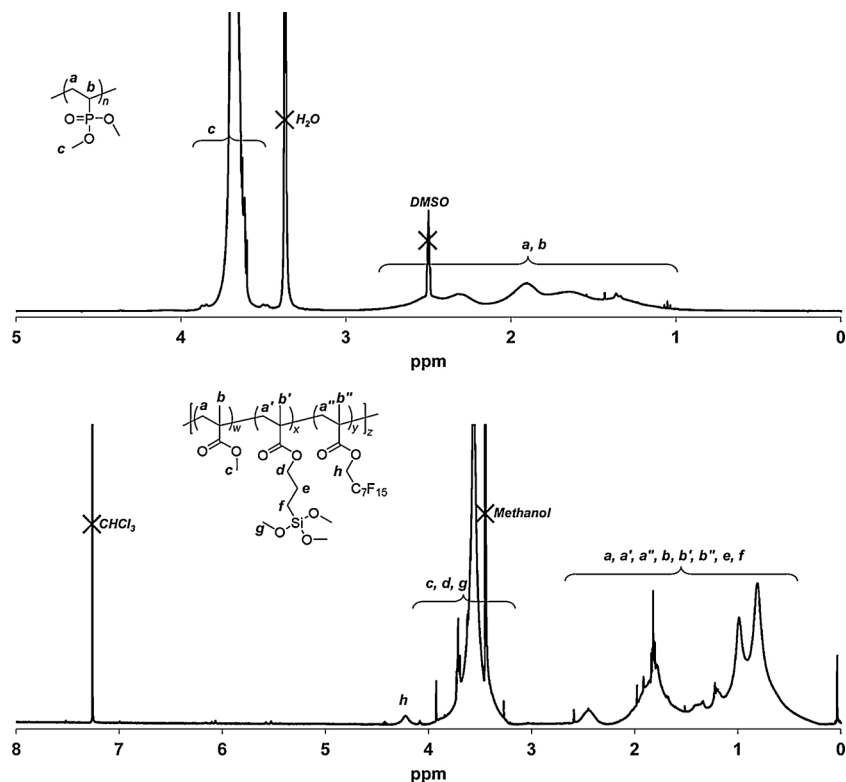


Fig. 3. ^1H NMR spectra of P(MVP) (in DMSO- D_6) and P(MMA/Si/F) (in CDCl_3) obtained by radical polymerization using AIBN.

Table 2

List of conditions used for the treatment of flax fabrics and change in weight after impregnation (in comparison to initial weight) for different conditions of solvent and duration, and after a radiation grafting procedure.

Sample	Impregnation conditions				Change in weight (%)	
	Treatment agent	Concentration (wt%)	Solvent	Duration (min)	After impregnation	After irradiation/washing
(1.a)	MVP	10	THF	1	5.6	–
(1.b)		5	Ethanol	1	6.6	–
(1.c)		5		5	6.9	–
(1.d)		5		10	7.4	–
(1.e)		5		20	8.5	–
(2.a)	MAPC1	5	THF	1	5.4	–
(2.b)		5		5	5.5	–
(2.c)		5		10	6.9	–
(2.d)		5		20	8.7	–
(2.e)		10		1	12.7	–
(2.f)		5	Ethanol	1	9.3	–
(2.g)		10			14.7	–
(3.a)	P(MVP)	10	THF	1	1.1	–
(3.b)		10	Ethanol	1	13.1	–
(3.c)		10		5	14.1	–
(3.d)		10		10	14.2	–
(3.e)		10		20	15.7	–
(4.a)	P(MMA/Si/F)	5	THF	1	10.8	–
(4.b)		10			18.8	–
(5.i)	Step 1: MAPC1	10	THF	1	12.7	1.4
(5.ii)	Step 2: MVP	10	THF	1	1.3*	0.6*
(6.i)	Step 1: MVP	10	THF	1	5.6	2.8
(6.ii)	Step 2: MAPC1	10	THF	1	8.5*	3.8*
(7)	P(MVP)/P(MMA/Si/F)	5/5	THF	1	–	–
(8)	P(Si-F/Si-V)	5	THF	1	–	–
(9)	MVP/P(Si-F/Si-V)	5/5	THF	1	–	–

* Weight gain was calculated in comparison with the modified flax obtained after the first step.

2.4. Characterizations

2.4.1. Inductively coupled plasma atomic emission spectroscopy

For some samples the phosphorus content was measured. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used and measurements were carried out by SGS Multilab.

2.4.2. Scanning electron microscopy / energy dispersive X-ray spectroscopy

Fiber micrographs were obtained using an environmental scanning electron microscope, SEM, (FEI Quanta 200). Fibers were deposited on an adhesive wafer and then cut with a scalpel so that the cross-sections are located at the edge of the wafer. Samples were metallized in a high vacuum sputtering metallizer (Bal-Tec CED 030, Balzers) in order to avoid their charging during analysis. The prepared fibers were then analyzed using a vertical sample holder and micrographs were obtained under high vacuum at a voltage of 12.5 kV, with a working distance of 10 mm. The SEM is equipped with an energy dispersive X-ray spectroscopy (Oxford INCA Energy system) which was used to determine phosphorus, fluorine and silicon location in the flax fibers.

2.4.3. ¹H NMR spectroscopy

NMR spectra were recorded with BrukerAC400 instruments, using deuterated chloroform or dimethyl sulfoxide as solvent and tetramethylsilane as the references for ¹H nuclei. Chemical shifts are given in parts per million (ppm). The experimental conditions for recording ¹H NMR spectra were as follow: flip angle, 90°; acquisition time, 4.5 s; pulse delay, 2 s; number of scans, 16.

3. Results and discussion

Self-extinguishing flax fabrics can be easily prepared by the procedure already described by Sonnier et al. (Sonnier et al., 2015). Briefly the fabric is firstly dipped into a solution containing the phosphorus monomer. After drying to remove the solvent, the monomer is grafted by irradiation through radical mechanism. Washing steps allow

removing the excess of unreacted molecules. The key step of the procedure is the first one, i.e. the dipping into the solution. Indeed, diffusion of the monomer into the fiber bulk must occur to ensure high radiation-grafted phosphorus content but also high grafting efficiency (defined as the ratio between the grafted monomer content at the end of the procedure and the absorbed monomer content measured at the end of the first step). Fig. 4 shows the grafting efficiency of two phosphorus monomers versus their concentration into the solution (THF solvent). Radiation dose was fixed to 50 kGy. Grafting efficiency increases continuously when increasing MVP content into THF. This is due to the diffusion of MVP from the surface to the core of flax fibers. Therefore there is no limitation to the absorbed amount of MVP. Almost all molecules (up to more than 90%) are grafted or homopolymerized after irradiation and cannot be removed by washing. On the contrary, MAPC1 is unable to diffuse into the bulk and is located essentially at the

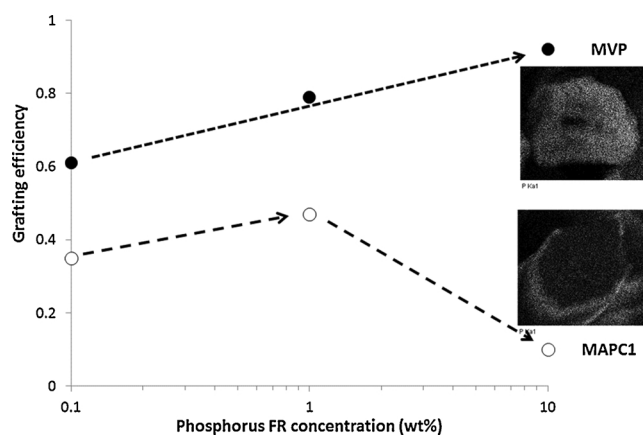


Fig. 4. Grafting efficiency of MVP or MAPC1 versus FR concentration into THF (radiation dose 50 kGy) – Pictures correspond to phosphorus mapping observed by SEM-EDX.

surface as observed in Fig. 4. Indeed the phosphorus mapping of the treated fibers shows a thin layer on their surface corresponding to the presence of the grafting agent. Even if the adsorbed amount increases when increasing the MAPC1 concentration, most of molecules are not grafted during irradiation and are easily removed during washing. Therefore grafting efficiency remains low to moderate and decreases for high MAPC1 concentration.

As evidenced in our previous paper (Sonnier et al., 2015), the main parameter allowing a fine control of phosphorus content is the FR concentration into the solution. Low radiation dose (10 kGy) is high enough to ensure an efficient grafting without degrading mechanical properties of flax fibers. Indeed, we showed that grafting rates for MVP and MAPC1 at 10 kGy are very close to those obtained at 20, 50 and 100 kGy.

3.1. Parameters influencing the location of the grafting agent

As explained in the previous section, diffusion of FR into the fiber bulk during the impregnation step is needed to obtain self-extinguishing fabrics with high grafted phosphorus contents. The objective of the present section is to identify the parameters allowing such diffusion. A large set of experiment conditions (including nature and size of molecules, solvent, impregnation duration) was investigated and SEM-EDX observations were used to assess the diffusion during the impregnation step.

3.1.1. Influence of the grafting agent nature

In this first part, the influence of the treatment agent nature on the location in the flax fiber structure was studied. Two monomers MVP and MAPC1 were tested in combination with THF. Other phosphorus molecules were also tested with water as solvent. These results can be found elsewhere (Hajj et al., 2018). The flax fabrics were dipped in a solution of THF containing 10 wt% of the grafting agent, for one minute at ambient temperature. This procedure is considered as the typical one. After drying, the samples were analyzed by SEM. Fig. 5 shows the cross section of flax fibers treated with MVP and MAPC1 (respectively (a) and (c)). Phosphorus is located mainly at the elementary fibers surface for MAPC1 whereas it is present throughout the whole cross section of the fibers modified with MVP (Fig. 5 (b) and (d)). The monomers structures are similar (in particular their size is very close) but they exhibit a different ability to pass through the different cell walls of the elementary fibers. This result proves that for these molecules a small size is not always sufficient to allow them to penetrate until the elementary fibers core. We assume that the affinities between the grafting molecule, the solvent and the flax components are the main parameters which control the diffusion into the fiber. In the following sections, several experiments were carried out to verify this hypothesis.

3.1.2. Influence of the molecule size

MVP was also homopolymerized before preparing the solution in order to study the influence of the molecule size on the diffusion. The affinity with THF for the synthesized P(MVP) is less good than MVP. Indeed the P(MVP)/THF solution has a cloudy appearance. Whereas the monomer penetrates easily in the elementary flax fiber (Fig. 5.b) the homopolymer is concentrated at the surface when applying the same conditions (Fig. 5.h). The macromolecular structure of the treatment agent could explain this non-negligible effect on the diffusion with a reduction of the transfer of P(MVP) through the wall of fibers. The change of affinity with the solvent can also explain this change of migration for P(MVP) in comparison to MVP.

P(MMA/Si/F) is another macromolecule used in this work obtained by the radical copolymerization of MMA, MPS and C₇F₁₅CH₂MA. This macromolecule was synthesized for this study to facilitate its characterization in the fiber by silicon and fluorine mapping using SEM/EDX analysis. The copolymer structure corresponds to a molar rate of monomers MMA/MPS/C₇F₁₅CH₂MA equal to 80/10/10. The same

conditions of concentration and solvent were used for the impregnation step. As evidenced by fluorine and silicon mappings (Fig. 6.b and c), in this case the terpolymer has succeeded to diffuse from the surface to the fiber bulk. Then the penetration of some macromolecules into flax fiber is still possible and a large size of molecules does not systematically inhibit the diffusion.

3.1.3. Influence of the impregnation duration

Diffusion depends on the nature and the size of the molecule. From the previous experiments, a question arises: is the diffusion inhibited or only slowed down in the case of MAPC1 in THF for example?

In order to study the influence of the impregnation duration, a flax fabric sample was dipped into a solution of MAPC1 in THF for twenty minutes. After drying, the sample was then analyzed by SEM-EDX to characterize the location of the phosphorus molecule. Fig. 7 shows the mapping of the phosphorus element for impregnation durations of 10 and 20 min. It can be observed that MAPC1 diffuses slowly into fiber bulk. After 10 min, the penetration of the molecule is obvious. When existing, the lumens are already filled while the phosphorus content into the bulk is still low. This observation means that the diffusion of the molecules can start from the surface or alternatively from the lumen. The presence of phosphorus is homogeneous throughout the whole section of the elementary fiber after 20 min. This result proves the importance of the duration of this step when the diffusion rate is low. For short times, MAPC1 combined with THF has not time enough to penetrate into the fiber bulk. However the comparison of the weight gain for flax fibers after 1, 5, 10 and 20 min of dipping for MAPC1/THF, MVP/ethanol and P(MVP)/ethanol shows a linear increase for the three systems (Fig. 8). We can observe that this weight gain is already high after 1 min of impregnation and the comparison of this gain with the final one after 20 min gives an increase of 61%, 29% and 20% for MAPC1/THF, MVP/ethanol and P(MVP)/ethanol respectively. So, the MAPC1/THF system which is supposed to have the worst solvent/treatment agent affinity shows the highest increase of weight gain between 1 and 20 min. This is supposed to be due to the slow diffusion of MAPC1 in the fibers structure corresponding to a progressive penetration of the molecule into the elementary fibers until the core.

3.1.4. Influence of the solvent

A too slow diffusion may be detrimental from an industrial point of view. It may be assumed that the diffusion rate is directly related to the affinity between the molecule and the solvent. Ethanol was used in combination with MAPC1 and P(MVP) to replace THF. As already observed, these grafting agents were stopped at the surface of the elementary fibers when combined with THF. But the combination with ethanol modifies the penetration of these molecules in the fibers (Fig. 5.f and j). Indeed we can observe the presence of phosphorus homogeneously dispersed in the cross section of the elementary fibers even if the P(MVP) concentration remains higher at the fiber surface. We assume that the change of the solvent used for the impregnation step involves an improvement of the affinity of the solvent/grafting agent couple. This better affinity allows the diffusion of the grafting agent through the primary wall of the elementary fibers until the core.

Other mixtures were also tested and the combinations of MVP or MAPC1 with acetone or toluene show the diffusion of the treatment agent in the whole structure of the fibers. Hajj et al. show also a homogenous diffusion of MAPC1 and MVP in the elementary flax fibers when water was used as solvent for the impregnation step (Hajj et al., 2018).

3.2. Multifunctionalization of flax fibers

We have shown that diffusion of molecules can be easily controlled by a suitable choice of impregnation conditions. On the basis of these results we developed two new strategies to modify regioselectively flax fibers. The aim of this work was to introduce in the fibers structure two

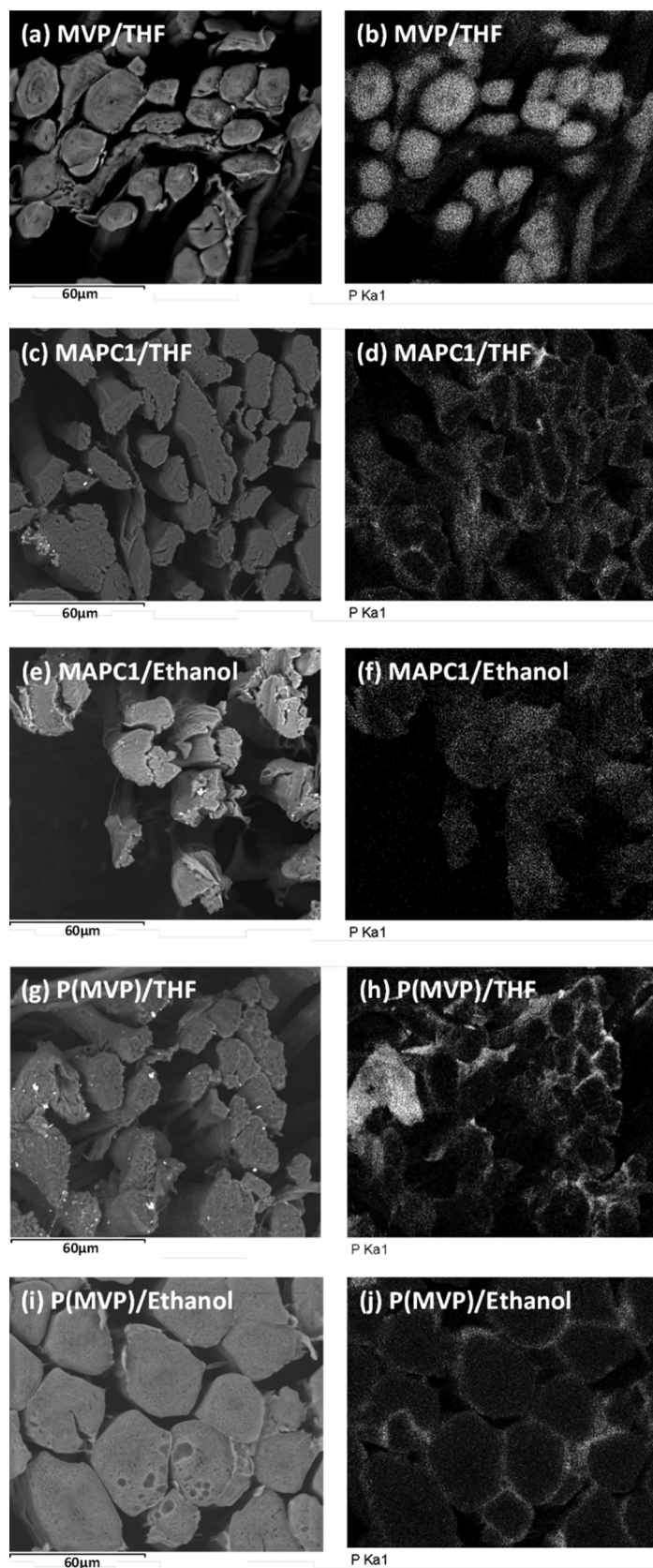


Fig. 5. SEM observations of flax fibers impregnated by solutions of (a) MVP, (c and e) MAPC1 or (g and i) P(MVP) in THF or ethanol (respectively samples 1.a, 2.e, 2.g, 3.a and 3.b from top to bottom) and (b, d, f, h and j) corresponding phosphorus imaging using EDX analysis.

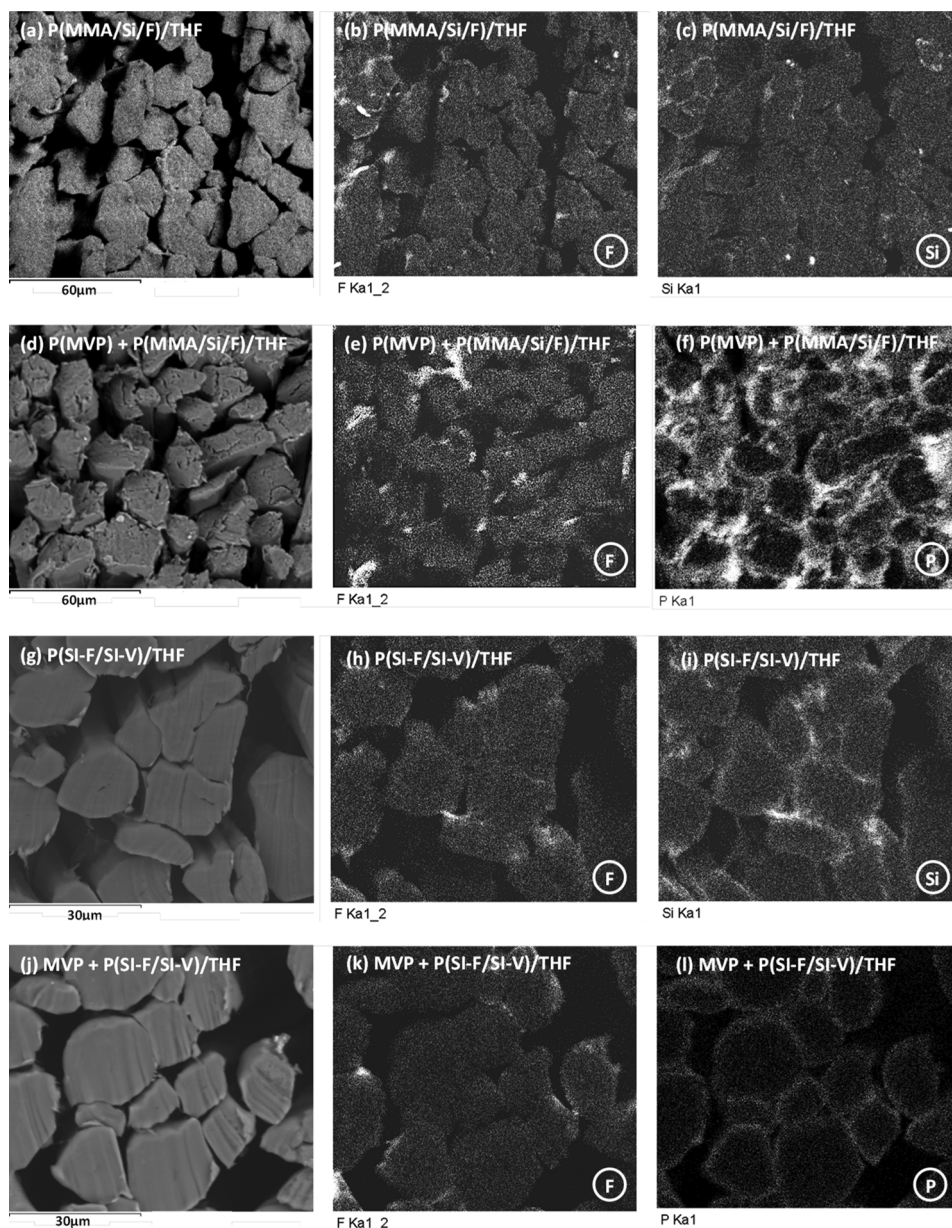


Fig. 6. (a, d, g and j) SEM observations of flax fibers impregnated by solutions of P(MMA/Si/F) or [P(MVP) + P(MMA/Si/F)] or P(Si-F/Si-V) or [MVP + P(Si-F/Si-V)] in THF (respectively samples 4.a, 7, 8 and 9 from top to bottom); (b, e, h, k) fluorine, (c and i) silicon and (f and l) phosphorus imaging using EDX analysis.

different molecules or macromolecules with location control. The first procedure is a multi-step procedure based on two successive impregnation/radiation-grafting/washing steps. The second one is a one-step procedure based on an impregnation step with a multicomponent solution.

3.2.1. Multi-step procedure

This protocol described in Fig. 9 is composed of two successive impregnation/radiation/washing cycles. For the first one, MAPC1 was combined with THF to introduce it only at the elementary fiber surface. As expected, after irradiation and washing the SEM analysis shows the presence of phosphorus essentially at the surface of the fibers (Fig. 10.a and b). This modified sample was then impregnated with a solution of MVP in THF to introduce it into fiber bulk. The SEM images show once again the presence of a high concentration of phosphorus at surface (Fig. 10.c and d) but we can observe also phosphorus inside the elementary fibers.

However phosphorus mapping reveals that phosphorus content is

much higher in surface than in bulk in contradiction to the results for functionalized fibers with MVP only. The values of change in weight after fibers washing are about + 1.4 wt% for MAPC1 and + 0.6 wt% for MVP. It may be assumed that the presence of MAPC1 on fiber surface does not prevent but slowdowns in some extent the diffusion of MVP into fiber bulk. This assumption needs further work.

The same protocol was used but inverting the monomers for each step: MVP was first used and then MAPC1. Higher grafting rates were obtained than when MAPC1 was firstly grafted (Table 2). The values of change in weight after fibers washing are about + 2.8 wt% for MVP and + 3.8 wt% for MAPC1.

So the order of the introduction of the monomers into the fibers is essential. MAPC1 seems to limit the diffusion of MVP when it is grafted first whereas MVP used for the first radiation grafting procedure may promote the diffusion of MAPC1. Indeed when MAPC1 is used for the first step and MVP for the second one the final weight gain (corresponding to the total grafting agent proportion) is about 2.0% whereas it is about 6.6% when the procedure is reversed. The final MAPC1

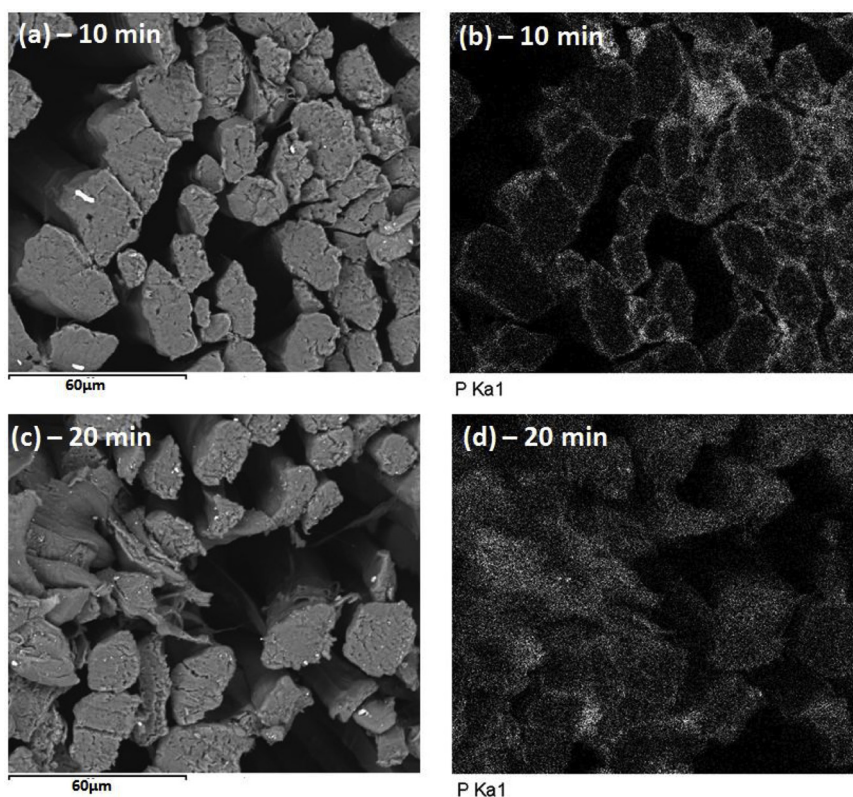


Fig. 7. Phosphorus mappings of flax fibers dipped into a solution of MAPC1 (5 wt%) in THF for various impregnation durations: (a) 10 min and (b) 20 min (samples 2.c and 2.d respectively).

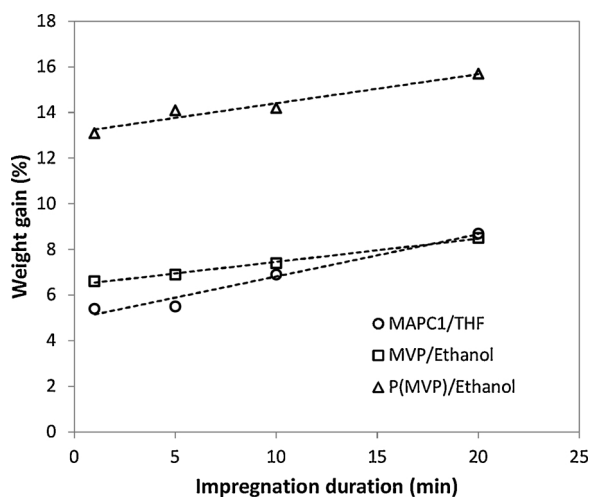


Fig. 8. Representation of the weight gain for flax fibers in function of the duration of the impregnation step for MAPC1/THF, MVP/ethanol and P(MVP)/ethanol systems.

proportion in flax is about 1.3 wt% when this treatment agent is used first whereas it is about 3.6 wt% when it is used in the second step.

3.2.2. One-step procedure

A more desirable way is to prepare multifunctionalized fabrics using a one-step procedure. The objective of this part is to introduce in the flax fibers two different treatment agents with a control of their location in the fiber using a one-step procedure (Fig. 11).

The first strategy is based on the use of two compounds which show different locations in the fiber when they are used alone. We used the homopolymer P(MVP) bearing phosphonated groups and P(MMA/Si/F)

bearing perfluorinated and silane groups. This copolymer allows mapping based on fluorine or silicon atoms and can evidence differences of location with the phosphonated homopolymer. As already shown, contrary to P(MVP), when flax is dipped into THF solution containing P (MMA/Si/F) alone, this macromolecule is present all over the cross-section of elementary fibers as evidenced by fluorine and silicon mappings (Fig. 6.b and c). When P(MVP) and P(MMA/Si/F) are coupled in THF, as expected we observe the presence of phosphorus only at the elementary fiber surface and fluorine and silicon throughout the cross section of the fiber (Fig. 6.e and f). However, a small fraction of P(MVP) seems to migrate into the bulk. It may be brought by the fluorinated terpolymer which diffuses itself and promotes the diffusion of P(MVP).

The second strategy is based on the use of two grafting agents able to penetrate in the bulk of elementary fibers when they are used alone with the same solvent (THF). Nevertheless, the combination of both agents in the same solution of THF disturbs the migration of one of both in the fiber. These treatment agents have poor affinity with each other and one of both has a lower affinity towards solvent. As a result its penetration into flax fiber is slower leading to regioselective functionalization. For this study, MVP was combined with a silicone product bearing fluorinated groups noted P(SI-F/SI-V) (Fig. 1). The use of MVP or P(SI-F/SI-V) with THF allowed the presence of the treatment agent in the bulk of elementary fibers (Fig. 5.a and Fig. 6.h and i respectively), whereas the combination of these two treatment agents in THF leads to different locations (Fig. 6.k and l). MVP is slightly present in the fiber bulk (Fig. 6.k) but is mainly observed at the surface whereas P(SI-F/SI-V) is homogeneously present in the whole section (Fig. 6.l). We assume that THF has more affinity with P(SI-F/SI-V) and the mixture THF/P(SI-F/SI-V) acts as a poor solvent for MVP, modifying its diffusion in the fiber structure.

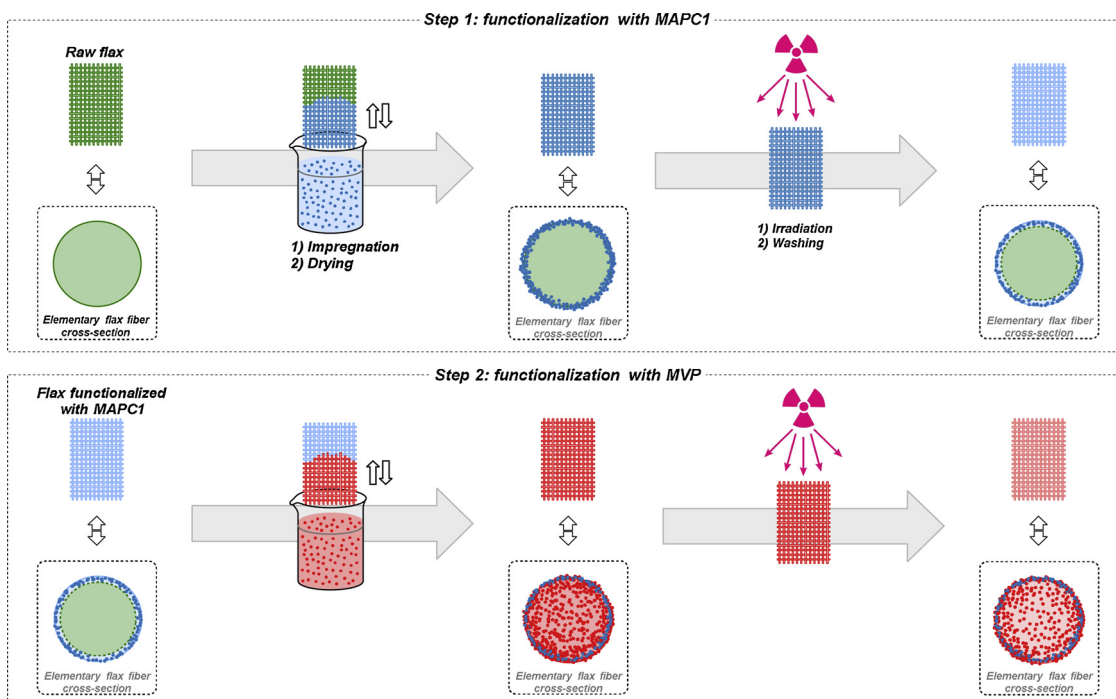


Fig. 9. Schematic representation of multi-step procedure for regioselective location of two grafting agents.

4. Conclusions

In this work, the link between the conditions used during the impregnation step of a radiation grafting procedure and the penetration and localization of treatment agents (molecules or macromolecules) into flax fibers structure was studied. For all studied molecules, the diffusion was always possible but its rate was dependent on a couple of parameters as the nature and the size of the molecules, the solvent, and

the impregnation duration. A suitable choice of these parameters allows locating the molecule on the elementary fiber surface or alternatively into the fiber bulk.

Regioselective location of molecules or macromolecules in the structure of elementary flax fibers was easily carried out by controlling the conditions of samples impregnation. Two original procedures were successfully developed for this purpose. The first one is a multi-step procedure based on successive impregnation/radiation-grafting/

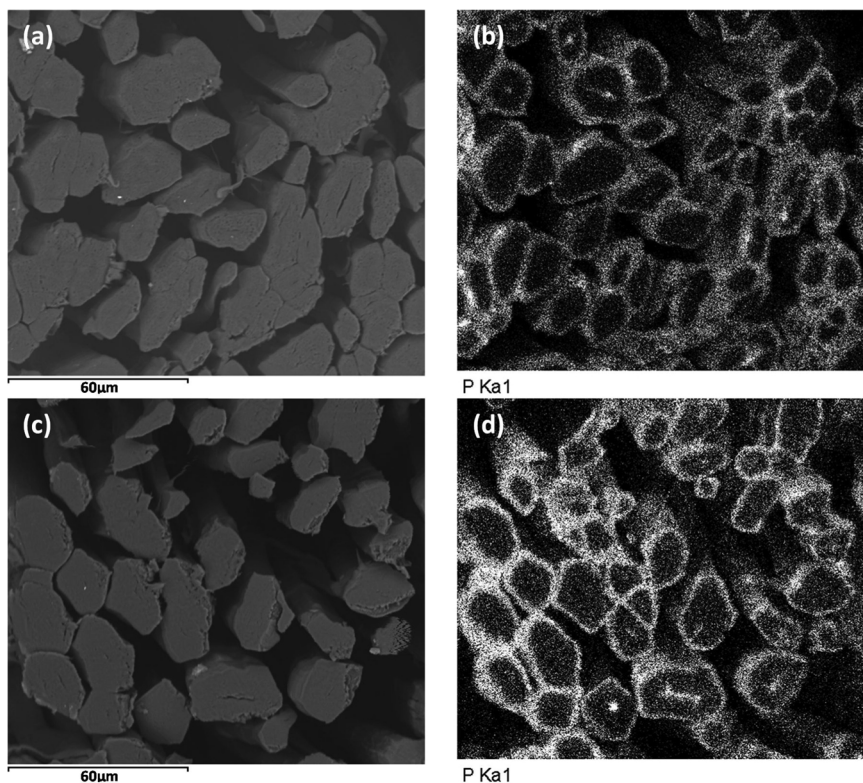


Fig. 10. (a) and (b) respectively SEM observations and phosphorus mapping using EDX analysis of flax fibers obtained after the first step of the multi-step procedure using MAPC1 (sample 5.i), (c) and (d) respectively SEM observations and phosphorus imaging using EDX analysis of flax fibers obtained after the second step of the multi-step procedure using MVP (sample 5.ii).

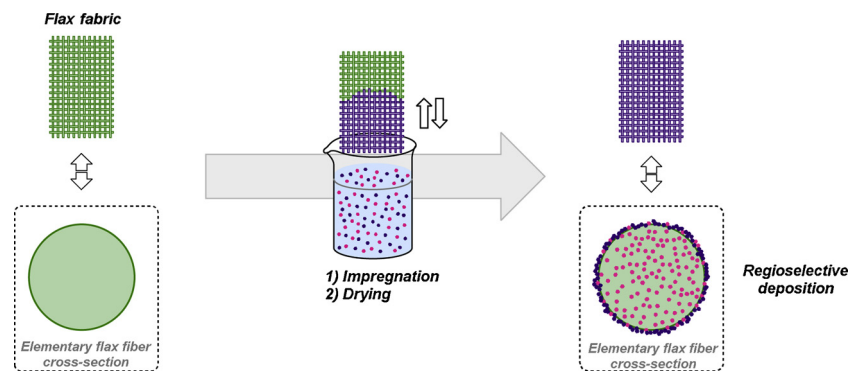


Fig. 11. Schematic representation of the one step procedure for regioselective deposition of two treatment agents in elementary flax fibers.

washing steps. The second one is a one-step procedure based on the use of a solution containing several components with different diffusion rates into fibers.

The accurate control of impregnation conditions should help to prepare highly multifunctionalized fibers through an easy process.

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