Modification of flax fiber fabrics by radiation grafting: application to epoxy thermosets and potentialities for silicone-natural fibers composites

Gabriela Tataru,[a] Kevin Guibert,[a] Marianne Labbé,[a] Romain Léger,[b] Sophie Rouif,[c,*] and Xavier Coqueret[a,*]

[a] Institut de Chimie Moléculaire de Reims, CNRS UMR 7312, Université de Reims Champagne-Ardenne, BP 1039, 51687 Reims, France

[b] LMGC, IMT Mines Alès, CNRS, Université de Montpellier, 6 Avenue de Clavières, 30319 Alès, France

[c] IONISOS, 69380 Civrieux d'Azergues, France

[*] Corresponding authors: sophie.rouif@ionisos.com, xavier.coqueret@univ-reims.fr

Abstract:

This article reports on the results of a collaborative work aiming at improving the mechanical performances of composites based on flax fabrics and epoxy thermosets or silicone materials. Radiation processing was assessed as a simple pretreatment to modify the surface composition of commercially available fabrics. Two approaches were explored after analysis of the chemical features of the two types of composites.

A first method designed for epoxy thermosets is based on the immobilization of bio-based adhesion promoters, partially epoxidized fatty oils exhibiting carbon-carbon unsaturations and epoxy groups expected to act as coupling agents after simultaneous EB radiation-grafting process.

The second method was based on the peroxidation by EB-irradiation in air of the flax fabrics selected for the reinforcement of vinylsiloxane-based silicone materials. The thermal

decomposition of peroxyl groups during the curing of a silicone matrix including vinylsiloxane units was indeed expected to generate covalent links between the fibers and reactive silicone formulations.

The advantage and limitations of the two methods are discussed based on mechanical testing of composite specimens fabricated with the original fabrics, or after implementation of the radiation-induced pre-treatments. The efficiency of the proposed grafting processes is supported by XPS at the different stages of the modification process, as well as by SEM observation of fractured samples. The spectroscopic signature of adhesion promoters for the epoxy composites or of models of the silicone matrix was observed after radiation-promoted immobilization and extensive washing of fabric samples.

Highlights

- Radiation-grafting of epoxidized seed oils onto flax fibers improves the properties of epoxy composites
- XPS supports the effective radiation-induced immobilization of adhesion promoters onto flax fibers
- SEM of fractured epoxy composites shows plastic deformation at the surface of modified fibers
- Radiation-induced peroxidation of flax fibers allows effective grafting of vinylsiloxanes

1. Introduction

Composites including natural fibers have recently emerged as a promising alternative to glass and synthetic fiber reinforced composites in various industries, particularly as structural materials for transport vehicles, packaging, building, leisure equipment and consumer goods sectors (Mohanty et al., 2005; Ahmad et al., 2019). The main perceived advantages are expressed both in terms of enhanced composite performance to weight ratio, as well as in reduced feedstock and lower environmental footprint of the fabrication process. Additional benefits arise from, low cost, low abrasiveness, good damping properties and biodegradability of the natural fibers (Pickering et al., 2016).

Despite the high specific mechanical properties of various natural fibers evaluated through laboratory experiments (Lamy and Baley, 2000), the corresponding composite materials with thermoplastic or thermoset matrices generally fail to reach the expected levels of performance. The limited thermal stability of natural fibers, the dependence of their properties as a function of their moisture content (Davies and Bruce, 1998), and the loss of their integrity during manufacturing restrict the processing conditions for manufacturing advanced composite materials. In addition, the mechanical properties of composites including natural fibers suffer from the weak physico-chemical interactions at the fibre - matrix interface, whereas the mechanical interlocks expected from the rough surface topography of the fibers does not result in effective transfer of mechanical load (Lamy and Pomel, 2002; Ku et al., 2011).

Various strategies have been proposed and evaluated to improve the interfacial adhesion between the components of the composite materials which is dependent on the differences in polarity between the fibers and the thermoplastic matrix, or of the precursors of the matrix in the case of thermosets or rubbers, and, after wetting, of ability for the fibers to develop

cohesive interactions through polar, H-bonding or covalent linkages through the functional groups present at the fibers surface (Mohanty et al., 2001; Smitthipong et al., 2014).

To overcome the presence of weakly bonded natural components remaining after retting and fiber isolation, or of textile processing additives used later in the process, cleaning and etching by wet chemical processes (Li et al., 2007) as well as by plasma treatments (Sun, 2016) can be considered as subtractive methods for improving the interfacial properties in composites.

Hydrophobic treatments and surface functionalization have also been performed to limit the water uptake of the fibres and/or to introduce various chemical groups favouring physico-chemical or covalent bonding between the modified fibers and the matrix (Simionescu and Denes, 1980; Ragoubi et al., 2010; Li et al., 2011; Azam et al., 2016).

Radiation-induced graft polymerization (Bhattacharya and Misra, 2004) has also been considered as a method to modify natural fibres with various types of polymers conferring them new surface properties and / or chemical reactivity (Rodriguez et al., 1977; LeMoigne et al., 2017). Such modification methods have been primarily developed to upgrade cotton textiles (Shahid-ul-Islam and Faqeer, 2015), or to produce natural fiber fabrics exhibiting metal retention properties of interest for environmental applications (Wojnarovits et al., 2010; Othman et al., 2019).

Graft polymerization can be performed using three basic methods exploiting the generation of free radical species in the substrate and, in some instances, also in the surrounding reactive medium, as depicted in Scheme 1 (Bhardwaj et al., 2014).

The mutual irradiation procedure (method a) consists in irradiating simultaneously the substrate and the monomer either in the vapour state, in solution or as a neat liquid. In the pre-

irradiation method (method b), the substrate is treated in vacuum or inert atmosphere followed by immediate or delayed contact with the monomer.
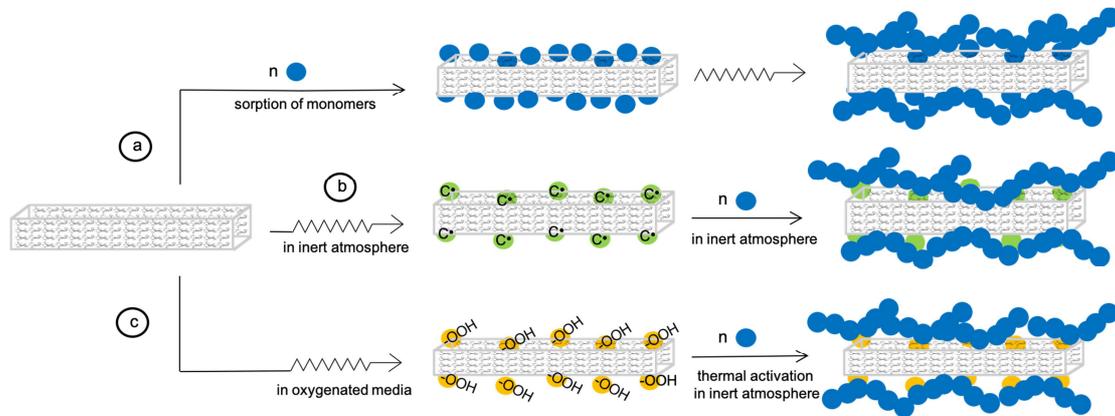
Scheme 1 – Sketch representing the three basic graft polymerization methods using high energy radiation: (a) mutual grafting or simultaneous process, (b) in situ generation of long-lived C-centered free radicals and (c) peroxidation.

In the peroxidation variant (method c), pre-irradiation is conducted in the presence of oxygen, generally in air, or in oxygenated media, to convert the formed free radicals into peroxides and hydroperoxides that will be used as thermal or redox-initiators in a subsequent stage for triggering the graft polymerization under inert conditions. These three methods have their specific advantages, drawbacks which will be discussed below in terms of chemical effects and technological implementation. However, considering the application to lignocellulosic materials, the three methods are all subject to the same constraint of minimizing the radiation dose to limit the loss of fibers mechanical properties caused by the scission of cellulose chains.

In the frame of a collaborative project aiming at the development of radiation-assisted modification of flax-fiber fabrics for composite materials based on simultaneous grafting and peroxidation, we have considered two approaches. The first method (method a of Scheme 1) was designed for epoxy thermosets and is based on the immobilization of bio-based adhesion

promoters, partially epoxidized fatty oils exhibiting carbon-carbon unsaturations and epoxy groups expected to act as coupling agents after simultaneous EB radiation-grafting process.

The second approach was based on the peroxidation by gamma or EB-irradiation in air of the flax fabrics selected for the reinforcement of silicone composite sheets (method c of Scheme 1). Pre-irradiation method is preferred when it is desirable to perform grafting away from the irradiation source as the active centers generated in the substrate can be preserved by storage at sub-ambient temperature. It is also suitable for gamma or EB irradiation for grafting at industrial scale (Makuuchi and Cheng, 2012; Drobny, 2013). The peroxidation method presents the additional advantage of simpler irradiation conditions without high-vacuum operations or without the use of inert gases. The thermal decomposition of peroxyl groups formed on the natural fiber fabric was expected here to generate covalent links between the fibers and the carbon-carbon unsaturation attached to components of the silicone formulations during the curing stage.

We report in this paper a selection of results illustrating specific aspects of the modification process using the two approaches, the positive effects observed on the properties of each type of composite materials and on the evidence of the grafting reactions at the molecular level.

2. Experimental

2.1 Materials

Three types of flax fabrics were used in this study: a proprietary flax taffeta (referred to as FTA) from Fibres Recherche Développement (Troyes, France), Rovinap LIN 67.08.VL36A (referred to as FUD), a proprietary fibrous material from Chomarat (Le Cheylard, France), with unidimensional flax fibers ($670 \ g \ m^{-2}$) associated with some glass fiber ($15 \ g \ m^{-2}$) as a warp, and glass fiber for the weft ($95 \ g \ m^{-2}$), all sewed on a thin non-woven polyester mat,

and Hexforce F1135-200 (referred to as FTW), a twill 2/2 fabric of surface density 200 g m^{-2} from Hexcel Composites (Les Asvenières, France).

The epoxy thermoset was a two-component mixture based on diglycidyl ether of bis-phenol A (DGEBA, commercial grade Ly1564 from Huntsman) blended just before use with 22.5 parts in weight of a isophorone-based polyamine hardener (Aradur 22962 from Huntsman) for 100 wt-parts of DGEBA.

Analytical grade solvents (ethanol, acetone) and 1,1,1,2,3,3,3-heptamethyl 2-vinyl trisiloxane were obtained from Sigma-Aldrich. Epoxidized linseed oil (ELO, Lankroflex E2447) with an epoxy content of 5.6 mmol g^{-1} was obtained from Akcros (UK).

2.2 Radiation treatments of flax fabrics

Peroxidation of flax fabrics for test experiments with vinylsiloxane model compounds was performed by irradiation in air using a 10 MeV Linac electron accelerator at an average dose rate of about 15 kGy s^{-1} (Ionisos, Chaumesnil). Peroxidized fabric samples were transferred in containers kept at -10°C and then stored at 4°C before use.

Pretreatments of flax fabrics for epoxy thermoset composites were performed with or without previous sorption of ELO by soaking the fabric in 2 % (wt./vol.) solution in ethanol of the adhesion promoter and drying in air to constant weight. Unless otherwise mentioned, the plain or ELO-sorbed cuttings were irradiated in sealed bags after deaeration by extensive flushing with argon, using a 10 MeV Linac electron accelerator at an average dose rate of 15 kGy s^{-1} (Ionisos, Chaumesnil). For absorbed radiation doses higher than 25 kGy, the treatment was fractionated in 25 kGy-passes to limit the rise in temperature associated with the radiation treatment. Irradiated fabric samples were used for composite fabrication within the next two days after irradiation.

2.3 Preparation of flax fabric-reinforced composites

Multilayered epoxy composites were prepared by vacuum-bag infusion of the epoxy-amine blend into an 8-ply pack of plain or modified Hexforce F1135-200 coupons of dimension 30 x 20 cm^2. The fabrics were dried from their moisture content by conditioning at 60-70°C for 16 h prior composite fabrication. The composite plates were cured within the vacuum bag placed in an oven for 15 min at 120 °C and then for 2 h at 150 °C. The glass transition of the matrix was typically measured by dynamic mechanical thermal analysis between 120 and 125°C.

Surface analysis by XPS

Surface composition of original and modified flax fabrics was determined by X-ray photoelectron spectrometry (XPS) using Kratos Axis Ultra DLD spectrometer operating with Al K$_\alpha$ monochromatic beam with an energy of 1486.6 eV. The spectra were recorded with a resolution of 0.55 eV and calibrated on aliphatic carbon C$_{1s}$ peak at a binding energy of 285 eV. Data processing was performed using CasaXPS software.

Mechanical testing

The tensile properties of the 8-plies epoxy composites were characterized using a Zwick / Roell Z020 machine equipped with a digital extensometer according to the ISO 527-4 standard. The plates were cut into 250 x 25 mm^2 test samples with the desired orientation (0° or 45°) with respect to the fiber direction. Test were repeated with 3-5 specimens to yield an average value of the tensile strength σ_B with a coefficient of variation between 2 and 5 %.

SEM

Scanning Electron Microscopy (SEM) was performed after fracture of epoxy composites at liquid nitrogen temperature using a FEI Quanta 200 FEB electron microscope.

3. Results and discussions

Immobilization of epoxy coupling agents on flax fabrics by simultaneous irradiation

To overcome the lack of compatibility between the surfaces of natural fiber and a typical epoxy thermoset cured with a isophorone diamine hardener, we have selected radiation-sensitive coupling agents derived from unsaturated seed oils. Epoxidized linseed and soya oils are commercially available in different grades with various carbon-carbon unsaturation and epoxy contents. The dual functionality of these bio-based compounds makes them good candidates for enabling radiation-induced free radical coupling to the natural fibers by addition on the olefinic moieties, whereas the epoxy function can react in a later stage with the amine component of the matrix (Scheme 2).
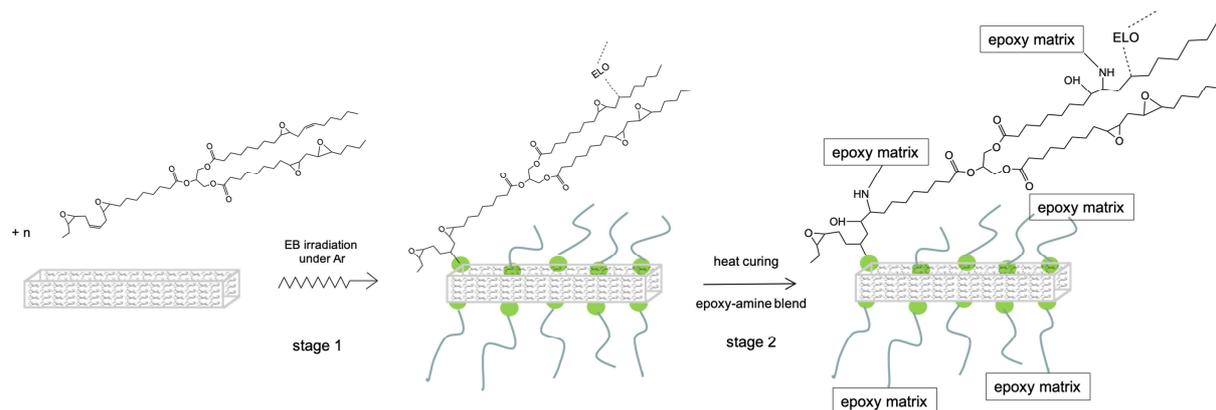
Scheme 2 – Sketch illustrating the principle of radiation-assisted attachment of epoxidized linseed oil onto natural fibers (stage 1), and the coupling between the matrix and the fibers through covalent linkages (stage 2).

Effective sorption of ELO on flax fabrics can be achieved by soaking the fibrous material into an ethanolic solution of the epoxy coupling agent (0.5 - 10 % in wt/vol) for various immersion times (5 - 120 min). For the present experiments, the concentration of the ELO solution was set to 2 % in wt/vol with a soaking time of 30 min. After drying at room temperature in a ventilated fume hood, the ELO uptake was 2.5 wt-% of the mass of the original fabric, a value somewhat higher than the amount of sizing for synthetic glass or carbon fibers (Broyles et al. 1998), but which takes into account the higher porosity of lignocellulosic fibers.

EB-treatment was preferred to γ irradiation for the mutual grafting of ELO and cellulosic fibers because of its advantages in terms of processing time and in initiation efficiency. The particular nature of the unsaturations in ELO induces a low reactivity in polymerization by free radical mechanism due to low homopropagation rate and to degenerative transfer reactions (Demchuk et al., 2016). The grafting experiments were therefore conducted at relatively high dose rate (average value of about 15 kGy s^{-1}) using a pulsed electron accelerator, the samples being packed in plastic bags sealed under argon to avoid quenching free radical reactions by molecular oxygen.

Increasing the dose applied to the fabric was shown to degrade the mechanical strength of the cellulosic substrate. The acceptable range was defined between 10 and 50 kGy, a trade-off between grafting efficiency and loss of expected reinforcing effect by the fibers being necessary. For a 20 kGy absorbed radiation dose, the amount of immobilized ELO was assessed by XPS analysis of the treated fibers submitted to a washing operation with acetone to remove the ungrafted ELO fraction.

The deconvolution of the high-resolution C1s XPS spectrum of Fig.1 (a) shows that the surface of the original cellulosic material contains a large amount of carbon atoms in the form of C-O observed at 286.5 eV, as expected for a polysaccharide constituted of anhydroglucose

units, but also, second in proportion, carbons with a peak centered on 285 eV that are not bound to O atoms (C-C) (Chilkoti and Ratner, 1993). This suggests strongly the presence of natural contaminants (lignin, fatty acid derivatives) or of textile additives (lubricants or process sizings) at the surface of the original fabrics, though the contribution of adventitious carbon species on materials with high surface energy is known to affect XPS spectra (Piao and McIntyre, 2002). This observation underlines the importance of a cleaning step in the preparation of high performance composite materials. The signals assigned for a ketal or carbonyl (C=O) or carboxyl (O-C=O) environments are also detected with the peaks at 287.9 and 289 eV, respectively.

The spectrum of Fig. 1 (b) unambiguously shows the dramatic change in chemical composition of the fiber surface after the grafting process and removal by desorption of ungrafted ELO by washing. The peak at 285 eV appears with a 3.5 times higher intensity than the one assigned to (C-O) carbons. The relative intensities of the signal assigned to ketal and carbonyl carbon atoms (C=O) compared to the acid and ester carbons (O-C=O) were inverted after surface modification with ELO. These two observations support the effective grafting of the coupling agent, which is rich in aliphatic and in ester carbon atoms. The high efficiency of the simultaneous grafting method with a 20 kGy-dose prompted us to compare the mechanical properties of composites prepared with the original and with the modified flax fabrics.
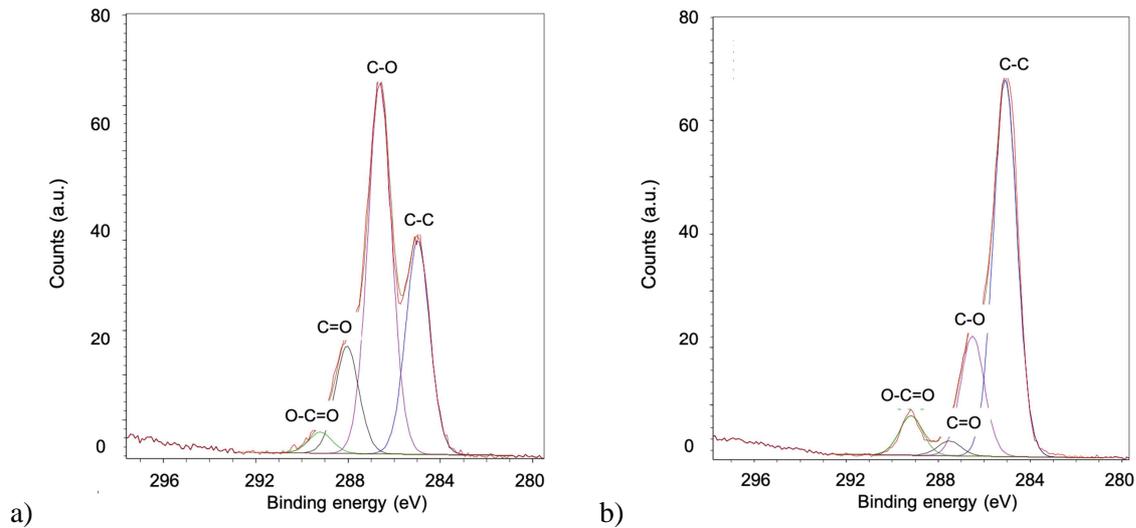
Figure 1 – High-resolution C1s XPS spectra of (a) acetone-washed flax fibers before treatment and (b) after sorption of ELO, EB-irradiation at 20 kGy and removal of ungrafted ELO (b).

Three sets of composite plates were thus prepared with the epoxy matrix using the two types of selected flax fiber reinforcements, FTW and FUD: a reference material including the original textile, a material with the textile irradiated at 25 kGy and a material with the radiation-grafted ELO coupling agent treated with the same EB absorbed radiation dose. The volume fraction of fibers in the composite was adjusted to 29.5 ± 0.5 % for FUD-reinforced plates of thickness 2.5 ± 0.05 mm, and 33.5 % for the FTW-reinforced ones with a thickness of 3.5 ± 0.05 mm.

The tensile strength (σ_B) measured for the 8-ply composite including the flax fabric elongated in the 45° direction with respect to the twill axes is significantly affected by the 25 kGy radiation treatment (Fig. 2). The decrease in tensile strength (11.3 MPa) represents a loss by more than 17 % caused by the irradiation on the cellulosic fibers. Composites including the ELO-modified flax fabric show the highest tensile strength in the series, therefore showing that the improvement of cohesive interactions at the fiber-matrix interface overcome the damage caused to the reinforcing component. The observed increased in σ_B value amounts to 7.7 MPa, with a standard deviation about 2 MPa, with respect to the composite including the

original fabric. This represents a relative increase of 11.7 %. With respect to the material prepared with a fabric irradiated at 25 kGy under argon, the relative increase in strength is close to 35 %.
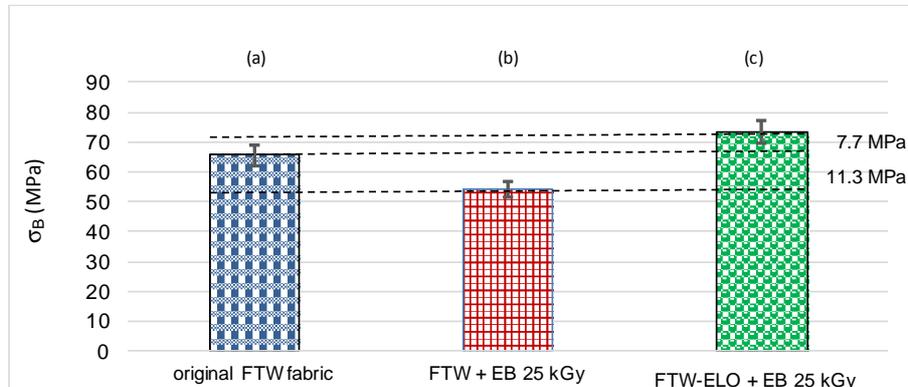

Figure 2 – Comparison of tensile strength for the 8-ply FTW-based epoxy composites measured in the 45° direction: (a) original fabric, (b) fabric after 25 kGy EB-treatment and (c) after sorption of ELO (2.5 wt-%) and subsequent EB-grafting at 25 kGy.

To correlate the effective improvement of mechanical properties to the efficiency at molecular level of the radiation-induced grafting of ELO, we have examined by scanning electron microscopy the profile of cryo-fractured samples taken from composite specimens prepared with the original fabric and with the ELO-modified fabric.

Scanning electron microscopy (SEM) pictures were taken to observe the imprint of the failure in the epoxy matrix and the polished cross-section of the fractured composite. Fig. 3 reveals two key morphological aspects in fractured composite samples including the unmodified fabric. Several long imprints are observed in the matrix (picture (a) of Fig. 3), corresponding to the location of the fibers that have been pulled out during the fracture. These imprints appear with a smooth surface, revealing the weak interactions between the fibers and the surrounding epoxy matrix. Many filaments are also observed and assigned to cellulosic microfibrils that may have been trapped in the matrix and torn off during the fracture (Carvelli et al., 2018), and/or that result from the sudden breaking of the fiber they were belonging to.

Examination of the cross-section picture in a non-fractured zone of a composite submitted to a breaking test (picture (b) of Fig. 3) confirms the weak interactions between the fibers and the epoxy matrix with the presence of void zones surrounding most of the fibers in the observed image.
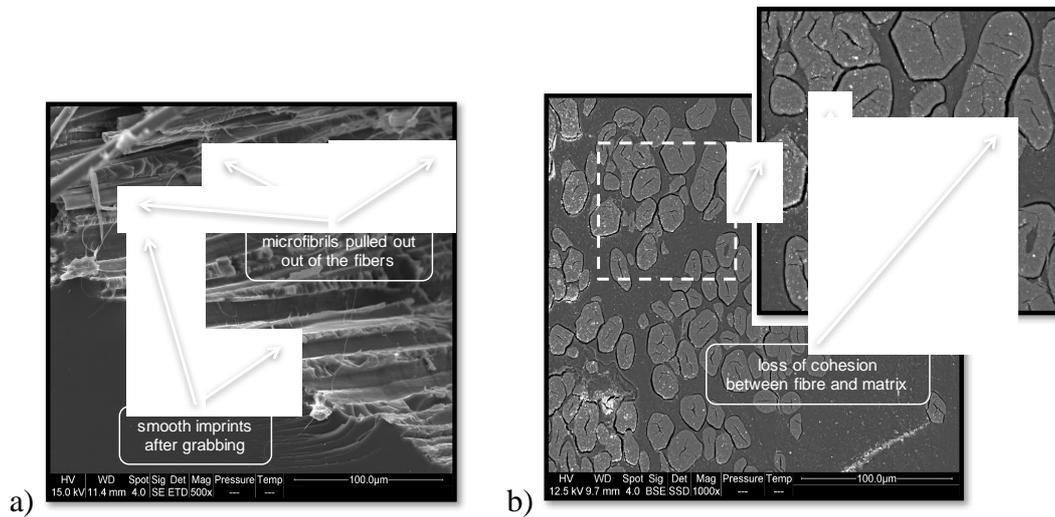

a)　　　　　　　　　　　　　　　　　b)

Figure 3 - SEM pictures of epoxy composites reinforced with untreated FTW fabric after fracture: (a) surface of the imprint in the matrix after grabbing of flax fibers, (b) polished crosscut showing the interface between fibers and surrounding matrix.

Samples prepared with a 2.5 wt-% level of ELO coupling agent grafted onto the fibers surface were also examined by SEM after a tensile test until breaking in the 45° direction with respect to the main axes of the twill fabric. Such a test at 45° produces a strong shear stress at the interface between the fibers and the matrix. We can observe in picture (a) of Fig. 4 some bridges between two fibers that result from the plastic deformation of the polymer material at the interface. In another zone of sample (picture (b) of Fig. 4), several bridges appear to have exceeded their plasticity limit and are broken all along the interface between the fiber and the matrix. Interestingly, in the same picture, unbroken bridges can be seen within a fiber. In comparison with the morphological aspects of the materials prepared with the unmodified FTW fabric, the formation of domains deformed and ultimately broken at the interface

provides a rational explanation to the improved properties of composites prepared with ELO-modified fabrics.
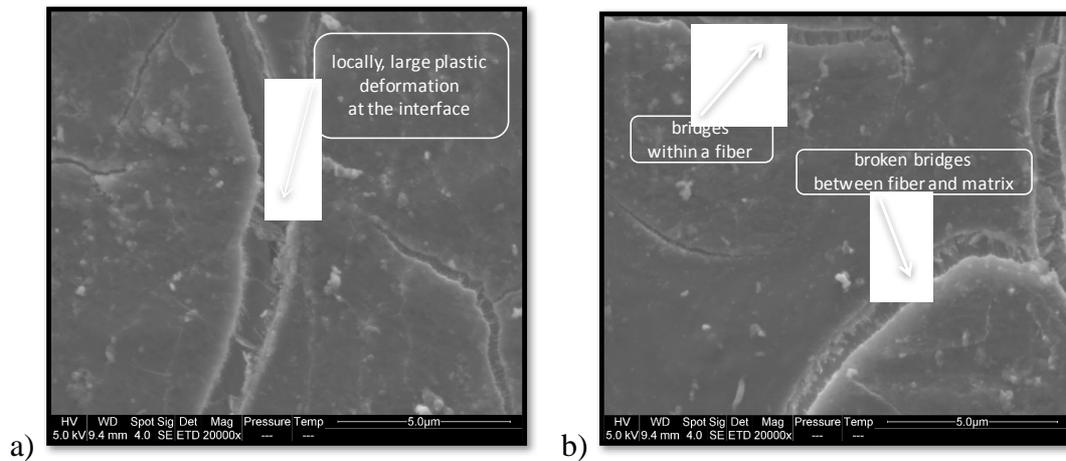

a) b)

Figure 4 - SEM micrographs of epoxy composites reinforced with flax fabric modified with ELO (2.5 wt-%) and by EB-irradiation (20 kGy) after tensile testing in the 45° orientation until breakage: (a) plastic deformation on the interphase between 2 fibers, and (b) broken bridges between one fiber and the matrix, and in other zones, plastically deformed bridges within a fiber.

Additional experiments were performed to examine the morphology of the composite prepared with a fabric modified by using larger amounts of ELO (2 to 16 wt-%) and by grafting. We present here picture (a) of Fig. 5 showing additional evidence of the formation of a ductile interphase between the fiber and the matrix. Moreover, picture (b) of Fig. 5 shows the formation of a crack within a fiber supporting an efficient transfer of the load to the fiber through the interphase.
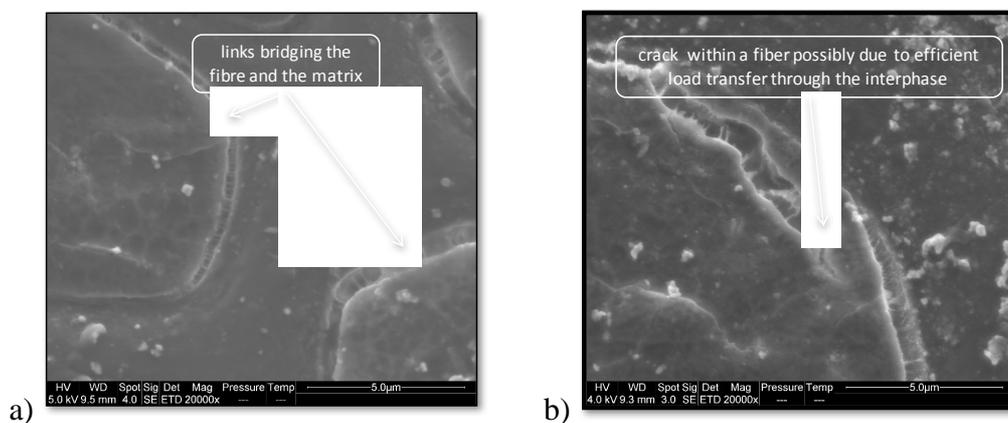

a) b)

Figure 5 - SEM micrographs of epoxy composites reinforced with flax fabric modified with ELO (16 wt-%) and by EB-irradiation (20 kGy) after tensile testing in the 0° orientation until breakage: (a) surface of matrix zone and (b) cross-cut of the tested specimen.

The tensile strength (σ_B) measured for the 2-ply composite including the FUD fibrous reinforcement elongated in the direction of the flax fiber yarns was shown to be weakened by the 25 kGy radiation treatment by 13 MPa (Fig. 6). The relative decrease in σ_B (-11.3 %) is lower than for the composites prepared with the FTW fabric (-17.2 %). The difference can be explained by the presence of a minor amount of glass fibers associated with the flax fibers in the main direction of the unbalanced FUD fabric.
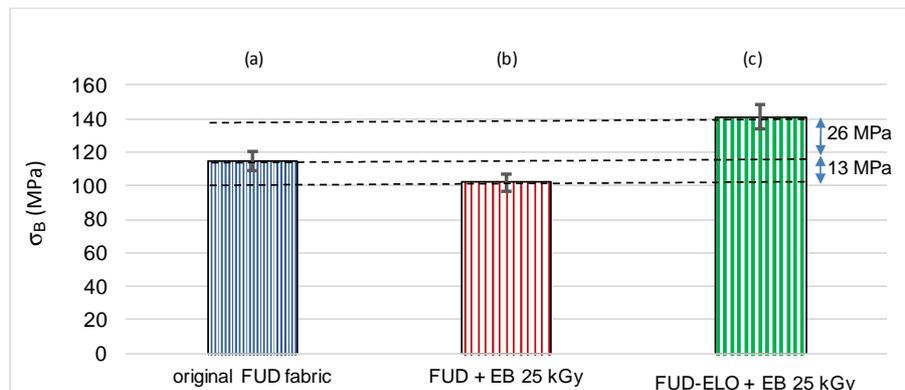

Figure 6 – Comparison of tensile strength for the 2-ply FUD-based epoxy composites measured in the main direction of the flax fibers: (a) original FUD fabric, (b) fabric after 25 kGy EB-treatment and (c) after sorption of ELO (2.5 wt-%) and subsequent EB-grafting at 25 kGy.

The positive effect of ELO grafting for a 2.5 wt-% sorption of the coupling agent represents a relative improvement of σ_B by 22.6 % with respect to the material containing the original fabric and by 38.2 % with respect to the irradiated fabric. These results confirm the potential of epoxidized vegetable oils as coupling agents for epoxy composites reinforced with natural fibers and the efficacy of radiation grafting by the simultaneous method for producing a reactive sizing covalently bound to the cellulosic fibers.

Peroxidation of flax fabrics by pre-irradiation

The peroxidation of flax fibers was considered as an alternative modification method for the production of silicone materials composites with improved properties (Class and Grasso, 1993). Pre-irradiation of the flax fabric in the presence of oxygen is expected to generate peroxyl groups that can be thermally activated at a later stage for achieving the covalent coupling of the vinylsiloxane-based material with the cellulosic fibers, as depicted in Scheme 3.
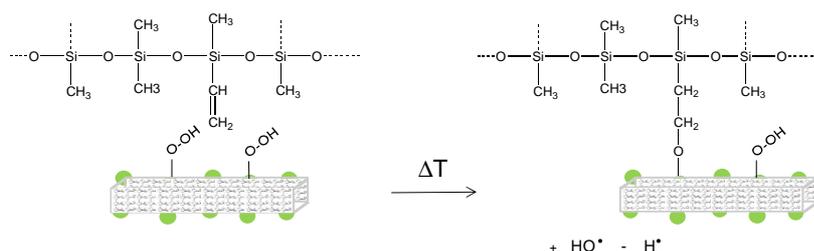
Scheme 3 – Sketch representing the grafting process based on the thermal activation of a peroxidized celllulosic substrate with a silicone matrix including vinylsiloxane units.

The three types of flax fibers were irradiated at various doses in air or under inert atmosphere to examine the changes in surface composition by XPS. The results showed qualitatively the same trends. The C1s signal of peroxides (C-O-O) is known to overlap with the peak of alcohols and ethers making it difficult to confirm the presence and to quantify peroxide compounds in this range of binding energy. However, peroxides were unambiguously evidenced in the O1s region of the spectrum with a new peak centered at 535.3 eV, a signal which was absent in the spectrum of the unirradiated fabric (Ward et al., 1979; Briggs et al. 2003). The high-resolution C1s spectrum shown in Fig. 7 was obtained from a FTA sample EB-irradiated at 50 kGy. The predominance of the (C-C) peak at 285 eV, also present in the unirradiated FTA samples, stresses the presence of non-cellulosic compounds at the surface.
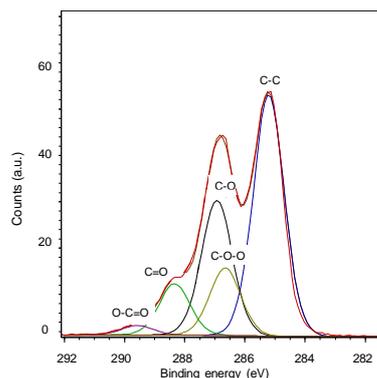
Figure 7 – High-resolution C1s XPS spectrum of FTA fibers after peroxidation by EB-irradiation at 50 kGy in air.

The deconvolution was performed by considering five distinct types of carbon atoms with C1s signals at 285.0, 286.0, 286.5, 287.9 and 289.0 eV, those already identified in the spectrum of Fig. 1 (a) (C-C, C-O, C=O, O-C=O) and a contribution of peroxidized carbon (C-O-O) assumed to be centered at 286 eV (Joshi and Friedrich, 2009; Joshi et al., 2011). The relative contributions of the different types of C atoms determined after the deconvolution are collected in Table 1.
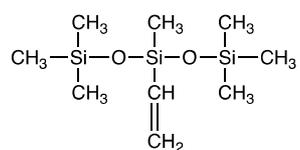
Table 1 - Assignment and relative contributions of C1s atoms in the XPS spectra of unirradiated FTA fabrics and EB-irradiated in air FTA fabrics.

Binding energy of C1s (eV)	285.0	286.0	286.5	287.9	289.0
assignment	C-C	C-O-O	C-O	C=O, O-C-O	O-C=O
unirradiated FTA	43.2 %	- %	27.0 %	6.1 %	1.1 %
FTA - 20kGy EB in air	44.1 %	7.6 %	17.3 %	6.2 %	2 .0%
FTA - 50kGy EB in air	35.3 %	9.7 %	19.9 %	7.4 %	1.4 %

Application to vinylsiloxane compounds

Silicone-fiber composites are a class of soft materials that have received relatively little attention despite the unique properties that can be expected from the association of the physical properties and chemical resistance of siloxane-based polymers with the mechanical performances of appropriate textile materials (Makami & Nakamura, 1984; Wu & Cai, 2013; Karthikeyan et al., 2017).

To assess the efficiency of a grafting approach using peroxidized fabrics with silicone resins including vinyl siloxane units that are present in various types of curable silicone elastomers (peroxide or radiation methods, hydrosilylation), evaluation tests were conducted with the vinylsiloxane model compound shown in Scheme 4 to perform analyses by XPS.

$$
\begin{array}{ccccccc}
& CH_3 & & CH_3 & & CH_3 & \\
& | & & | & & | & \\
CH_3\!-\!Si\!-\!O\!-\!Si\!-\!O\!-\!Si\!-\!CH_3 \\
& | & & | & & | & \\
& CH_3 & & CH & & CH_3 & \\
& & & \| & & & \\
& & & CH_2 & & &
\end{array}
$$

Scheme 4 – Structure of the model vinylsiloxane (1,1,1,2,3,3,3-heptamethyl 2-vinyl trisiloxane) used for grafting experiments onto peroxidized FTA fabric.

Depending on their chemical structure and composition, organic silicones give rise to Si2p XPS signals at binding energies around 103.5, 103, 102.5 and 101.5 eV, for $Si-(O-)_4$ (Q units), $R-Si-(O-)_3$ (T units), $(R-)_2-Si-(O-)_2$ (D units), and $(R-)_3-Si-O-$ (M units), respectively (Beamson and Briggs, 1992; Louette et al., 2005,).

We have recorded the XPS spectra of the FTA fabrics in the original state, after EB-irradiation at 50 kGy in air, after sorption of 3 wt-% of the model vinyltrisiloxane and grafting at 100°C, and then after washing. The corresponding spectra shown in Fig. 8 reveal that the surface of the original fabric already contains silicon atoms, assigned after deconvolution to Q and T units (broad peak around 103 eV), and a finer signal (around 102 eV) mainly D and M units (Fig. 8 (a)). After irradiation at 50 kGy in air, this part of the XPS spectrum is not significantly changed (Fig. 8 (b). After thermal grafting of the vinyltrisiloxane at 100°C for 1 h, the signal/noise ratio is significantly reduced, showing a much stronger contribution of M and D units (Fig. 8 (c)). After washing the fabric to remove the ungrafted siloxane with tetrahydrofuran, the recorded spectrum (Fig. 8 (d)) was quite similar to the previous one, confirming the high grafting yield achieved in these conditions. The atomic composition of the surface of the grafted fabric after washing was approximately: C (72.5 at-%), O (26.0 at-%) and Si (1.5 at-%), thus confirming that a large proportion of sorbed vinyltrisiloxane was effectively grafted onto the fibers.
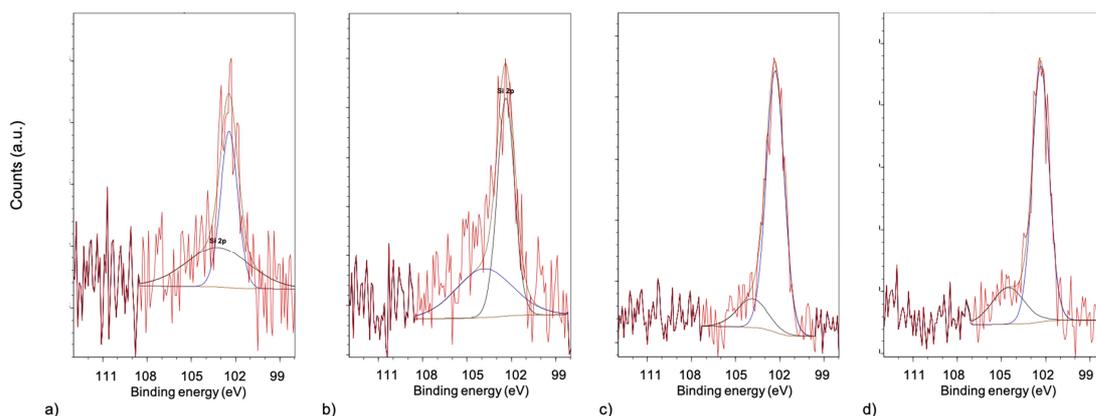
Figure 8 – High-resolution Si2p XPS spectra of FTA fibers, (a) in the unmodified state, (b) after peroxidation by 50 kGy EB irradiation, (c) after grafting of the vinyltrisiloxane by thermal reaction, and (d) after washing out of the ungrafted siloxane model compound.

Peroxidation appears an attractive process for the industrial manufacture of silicone elastomers natural fibers. Recent results illustrate the potentialities of this approach (Rouif et al., 2019).

The precise determination of the amount of peroxides in the fabrics as a function of storage time and conditions would help to gain a better understanding of the antagonism between the benefits of grafting and the loss of intrinsic properties of the reinforcing fabric. Initial measurements just after peroxidation and monitoring of the peroxide content upon ageing under various conditions would provide a better control over the process. We are currently working on the quantitative determination of peroxides in various types of irradiated cellulosic materials (Machat et al., 2019).

4. Conclusion

Analysis of the chemistry involved in the curing process of the two selected types of matrix, an epoxy thermoset and silicone materials bearing vinylsiloxane units, led us to explore two

radiation-mediated grafting methods applicable to commercial flax fabrics. Mutual irradiation and peroxidation by pre-irradiation were investigated to gain a better understanding of the key stages of each method and to evaluate their efficiency. The resulting chemical modifications occurring at molecular level were quantified by XPS analysis, a method providing a fine insight into the changes of fibers surface composition at the different stages of each modification method. Mutual grafting of ELO, an original bio-based coupling agent was shown to improve the performances of the epoxy thermoset composites. Pre-irradiation proved to be effective to induce the covalent attachment of vinylsiloxanes.

Some critical aspects were identified. As radiation-sensitive substrates were concerned, the radiation dose should be minimized. We have shown that significant levels of chemical modification can be achieved for radiation treatments at doses of 15-20 kGy, with favorable impact on the mechanical performances. The surface of the starting fibers or fabric which can be contaminated by non-cellulosic compounds, either naturally occurring components from the plant or from the retting process, or from textile processing additives. Variations in the contamination levels by the aforementioned compounds and in moisture contents in the starting materials may influence negatively the repeatability of the modification methods by surface grafting.

The peroxidation method is confirmed as convenient from an industrial viewpoint, since it allows to decouple the pre-irradiation stage from the application of chemical additives and from the fabrication of the composites, avoiding to manipulate chemical reagents in the irradiation facility. The preservation of peroxide functions and the precise control of their amount as a function of storage conditions and duration is a critical point requiring the development of specific quantification methods.

Mutual grafting of epoxidized plant oils onto flax fabrics, particularly ELO, an original bio-based coupling agent, was shown to allow for the formation of an interphase upon curing with an epoxy-amine thermoset matrix. SEM micrographs of fractured specimens confirmed the occurrence of load transfer between the fibers and the matrix. Significant, yet limited, improvement of the composite tensile strength by 10-20 % was demonstrated in comparison with the untreated fabric composite.

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