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Hajjar-Garreau

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TOWARDS MORE EFFICIENT AND ENVIRONMENTAL FRIENDLY FLAX-BASED ECO-COMPOSITE THROUGH DIRECT F₂ FLUORINATION AS A COMPATIBILIZATION TREATMENT

Olivier Téraube^{a,b}, Jean-Charles Agopian^{a,b}, Monica Francesca. Pucci^c, Pierre-Jacques Liotier^d, Nicolas Batisse^a, Samar Hajjar-Garreau^e, Karine Charlet^b Marc. Dubois^a

a: UCA, Clermont Auvergne INP, ICCF, BP 10448, 63000 Clermont-Ferrand, France

b: UCA, Clermont Auvergne INP, Institut Pascal, BP 10448, 63000 Clermont-Ferrand, France –

c: LMGC, IMT Mines Ales, Univ Montpellier, CNRS, Alès, France

d: Polymers Composites and Hybrids (PCH), IMT Mines Ales, Alès, France

e: IS2M, CNRS-UMR 7361, Université de Haute-Alsace, 68057 Mulhouse, France

olivier.teraube@uca.fr

Abstract: *Because of their specific properties, vegetal fibers are increasingly used as sustainable polymer reinforcements for eco-composites. Nevertheless, their polar character hinders them from being used more frequently at industrial scale due to their incompatibility with mostly dispersive polymers (the cheapest and most common ones). In this study, direct fluorination treatment was carried out to covalently graft fluorine atoms at the outmost surface of flax fibers, allowing the polarity of flax fibers to be significantly decreased. Thanks to this polarity reduction, the gap between the surface energies of the fibers and polymer matrix (epoxy) was reduced improving the wettability of the fibers during the infusion process. Thereby, porosity of the composite thus formed is significantly reduced, increasing its Young's modulus by 25%, its maximal flexural stress by 10% whereas the percentage of maximal elongation is decreased by 15%. These improvements are achieved without any chemical coupling agent or solvent harmful to the environment.*

Keywords: Vegetal fibers composite; Fluorination; Wettability; Interface; Porosity

1. Introduction

Vegetal fibers are increasingly used to substitute glass fibers for polymer strengthening to make eco-composites. Indeed, in addition to the fact that vegetal fibers and glass fibers present equivalent specific properties, the use of the former allows to valorize bio-based and local resources while lightening the overall weight and reducing the cost of composites. Therefore, all these advantages provide to vegetal fibers to be more and more used in the transport industry (aeronautics, automotive, etc.); this trend is expected to increase in light of current environmental issues and the emerging context of the bio-economy aimed at continuing economic growth while preserving the environment and earth resources.

However, one of the main difficulties arising when using these vegetal compounds as polymer matrix reinforcement is their incompatibility with a large part of the latter. Indeed, the hydrophilic nature of vegetal fibers makes them sensitive to moisture absorption and difficult to wet by hydrophobic resins (which represent the majority of polymer matrices used). This incompatibility results in a poor effective adhesion, partly due to micro-porosities, between fibers and matrix that would greatly weaken the mechanical performance of these eco-composites [1].

In order to obtain the optimal mechanical performance of these composites, it is often considered necessary to compatibilize these vegetal fibers with the polymer matrix. Over the years, several chemical and/or physical methods have been developed for this purpose (thermal treatment, electric discharge, acetylation, MAPP treatment, mercerization, etc. [2]). If these treatments allow to decrease the polarity of the fibers and thus to reduce the presence of cavities at the fiber/matrix interface, they are generally harmful for the environment because of the use of chemical reagent, solvent and/or a high energy cost, inducing in all cases an increase of the carbon footprint of the composites, which is incompatible with the very principle of "eco-composite" aiming at reducing as much as possible the environmental impact of these materials.

The fluorination treatment takes place in this context. Indeed, thanks to the reaction of molecular fluorine F_2 onto flax fibers surface (or any other lignocellulosic fibers [2,3]), it is possible to covalently graft fluorine by this chemical element. This treatment of natural fibers, carried out only at a laboratory scale up to now, allows the polarity of the substrate to be significantly decreased without modifying its bulk properties. Moreover, as a gas/solid reaction, fluorination is performed without using toxic solvent in a closed reactor, *i.e.* without release of any toxic substance in the atmosphere, and the reaction occurs spontaneously at room temperature; so this treatment exhibits a very low environmental footprint.

In addition, direct fluorination treatment is already an industrial process employed to treat commercial polymers in order to add the superficial properties of a fluoropolymer at the substrate surface [4,5]. Moreover, this method is fast, without any human contact with the reactant, reproducible, and thus presents all the advantages required for an eco-responsible industrial way to reduce the vegetal fibers' polarity in order to compatibilize this filler with hydrophobic polymer.

Thereby, the present work aims at carrying out fluorination of flax fibers at a semi-pilot scale in order to increase the quantity and size of fluorinated fibers per batch allowing the manufacture of eco-composites with long fiber reinforcement. Therefore, fluorinated flax fibers and epoxy resin (with a polar component typically measured below 5mN/m [6]) will be employed together *via* Composite Vacuum Resin Infusion, to form eco-composite. Those composites will be then tested by flexural test to evidence the enhancement of the mechanical performance of the fluorinated fillers based material as expected because of the fiber polarity reduction, according to the literature [1].

2. Materials and methods

2.1 Materials

Flax fibers were pieces of FlaxTapeTM 110, purchased from Eco-Technilin. These fibers which are 40cm width tape of unidirectional flax fibers with a weight of 110g/m² have undergone a fluorination treatment described below (noted "fluorinated"). For comparison, other fibers were used "as received" (noted "Raw" in the following) to make composite materials.

Composite were manufactured using an epoxy resin: resoltech 1050, coupled with 1056S hardener, both purchased from SF Composite. Resin and hardener were mixed together with a 100/35 weigh ratio.

2.2 Fluorination

Fluorination of flax fibers was performed inside a 50L passivated nickel reactor (covered with NiF₂) in static conditions. The flax fibers were distributed into the fluorination reactor over 4 trays, each being 65cm long and 21cm wide Figure 1a.

The reactive gas consists of a mixture of pure elemental fluorine, purchased from Solvay Fluor (less than 0.1 vol.% of admixtures, mainly oxygen) and pure Nitrogen (99,999 % purity). Before each reaction, fibers were first outgassed during 2h under primary vacuum (10⁻³ mbar) at 120 °C (setpoint) within the reactor. Then, the heating is turned off, and the reactor is left to cool down overnight.

After that, the chamber (still under primary vacuum, *i.e.* 10⁻³ bar) was filled with the gases. In a first step, N₂ is injected into the reactor during 5min at 400 mL/min flow rate. Then, the reactive F₂/N₂ mixture was introduced during 20 min in the reactor with N₂ and F₂ flow rates which are set at 400 and 100 mL/min, respectively. At the end of this step, the pressure inside the reactor is of 200mbar. Thereafter, N₂ is added (600mL/min) in the reactor until a pressure of 1 bar was reached. The reactor is then immediately flushed with pure nitrogen gas overnight to both stop the reaction and remove the traces of unreacted F₂, HF, CF₄, and C₂F₆ (those gases were removed by a soda lime trap). Finally, the fibers are once again outgassed for 1 h under nitrogen at 120 °C for the completion of removal of all fluorine-based gases from the sample surface.

2.3 Composite manufacturing

Composite plates are prepared by Composite Vacuum Resin Infusion (that we will call infusion afterwards). To manufacture these plates, a PMMA mold of 400mm long, 40mm wide and 3mm thick was used. For each infusion, 6 fibers (raw or fluorinated) plies are cut (length in the fiber direction) to the mold dimensions and placed within it (Figure 1b). Then, 2 cylindrical gaskets (in black on Figure 1b) are placed in the location provided, to ensure the vacuum tightness of the mold. After that, the counter mold is placed, and the 2 parts of the mold firmly closed and held in position thanks to C-clamps (Figure 1c). Thereafter, resin was mixed with its corresponding hardener and mixture was stirred for 5min. Once mixed, the resin pot is connected to the mold by a plastic pipe, and the whole infusion device was put under vacuum (10⁻³ bar). After 5 minutes, circuit upstream of the resin is returned to atmospheric pressure, while the mold is still under vacuum, driving the resin inside the mold. Once the infusion done, the set is left 24 hours to obtain a composite plate dried enough to be demolded. Then the plate is demolded and dried for, at least, 2 weeks at room temperature.

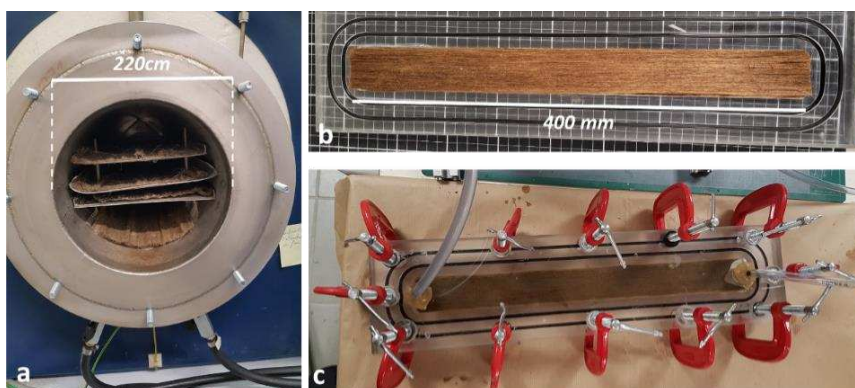


Figure 1: (a) 50L fluorination reactor with 4 trays inside ; (b) and (c) composite manufacturing

2.3 Characterization

FTIR experiments were carried out with a Nicolet 6700 FT-IR (Thermo Scientific) spectrometer in ATR mode. For each spectrum, 32 scans with 4 cm⁻¹ resolution were collected between 4000 and 524 cm⁻¹.

¹⁹F solid state NMR spectra were recorded using a 300 MHz Bruker Avance spectrometer. A magic-angle spinning (MAS) probe operating with 2.5 mm rotors was used allowing a 30 kHz spinning rate. A simple sequence was used with a single $\pi/2$ pulse with a duration of 4.0 μ s. ¹⁹F chemical shifts were externally referenced to CF₃COOH and then referenced to CFCl₃ ($\delta_{CF_3COOH} = -78.5$ ppm vs δ_{CFCl_3})

In order to estimate the change in the surface energy due to treatments, the determination of the contact angle between fibers and different liquids is necessary. To measure this contact angle, the most common method is the “sessile drop” technique [7]. However, this technique cannot be employed with fibers and fabrics, because of their shape and texture that induce a fakir effect distorting the measurements. Thereby, several methods have been developed along time in order to perform this measurement on single fibers [8–11]. Among them, the tensiometric one seems the most convenient. As described by Qiu *et al.*[9], it is based on the use of a Wilhelmy balance and the Wilhelmy relationship (1)

$$F = \gamma_l p \cos \theta \quad (1)$$

where F is the capillary force (mN), p (m) the wetted length, θ (°) the contact angle and γ_l (mN/m) the surface tension of the liquid.

Using the method described in Pucci *et al.* [12], measurements were performed using a Krüss K100SF tensiometer. To measure the contact angle with a given liquid, a single fiber was first extracted from the strips of fibers. This one was placed in a clamp within the tensiometer and placed as close as possible to a crystallizer filled with the liquid without touching it. This crystallizer moved at a speed of 1mm/min and came in contact with the fiber. Then it went up to a depth immersion of 5 mm, the tensiometer allowing to measure the capillary force exerted by the liquid on the fiber.

To determine the polar and the dispersive components of the surface energy of fibers, the Owens-Wendt method was considered [13]. This theory is based on the equation (2) that allows to determine the dispersive and polar components of the fiber surface energy (γ_s^d and γ_s^p).

$$\frac{\gamma_l(1 + \cos(\theta))}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p} \left(\frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}} \right) + \sqrt{\gamma_s^d} \quad (2)$$

For each sample, at least 5 measurements were carried out with different test liquids, and the mean value of θ was used to plot data. The uncertainties on surface energy components were measured using the maximum and minimum slopes techniques.

To evaluate the impact of the fluorination treatment on flexural properties, three points bending tests have been conducted following ASTM D790-03 [14]. However, only 4 samples

were tested instead of 5 because of the limited amount of space available on composites. Dimensions of the samples were 120×18×3mm³, and because the standard requires a span-to-death ratio larger than 16:1 at minimum and recommends it higher than 32:1, we have set our support span to 100mm (span-to-death ratio = 33:1). Experimentations were carried out on a Zwick UTS20K machine equipped with a 20 kN capacity load cell, at a crosshead displacement rate of 1 mm/min.

3. Result and discussion

3.1 Homogeneous fluorine grafting

Fluorination of flax fibers, as well as other lignocellulosics materials, is known to graft fluorine atoms at the outmost surface of these compounds in replacement of -OH groups [2,3]. Therefore, the fact that fluorination of lignocellulosic materials is possible were previously discussed in a previous paper [3,15].

According to the high reactivity of F₂ gas, the tubular geometry of the reactor with a gas injection on one side may result in inhomogeneous fluorination rate along the fibers during the scale-up with a reactor of 50L volume: chemical analysis of fibers must be carried out to check the homogeneity of the treatment. Figure 2 displays the IR and ¹⁹F NMR spectra of fluorinated flax fibers, as a function of the location of the fibers tape in the reactor. These spectra were recorded with samples collected at 0cm and 65cm from the edge, in the center of the fibers width (the 0cm side corresponding to the width closest to the fluorine insertion) on the 4 trays that were placed one above another into the reactor. The presence of bands on ¹⁹F NMR spectra demonstrates the covalent grafting of fluorine atoms at the flax fibers surface as already observed on previous work; formation of -CHF, -CF₂ and with less extend -CF₃ groups is then evidenced [16]. In addition, because of both the *quasi* overlapping of both ¹⁹F NMR and FT-IR lines whatever the location of the sample in the trays and the perfect similarity of these lines for the case in between 0 and 65cm, we clearly notice that treatment is chemically and quantitatively almost identical whatever the observed area. These results demonstrated that the chosen treatment conditions allow a high homogeneity over the whole length of the samples. This characteristic is a prerequisite for the use of the mechanical properties.

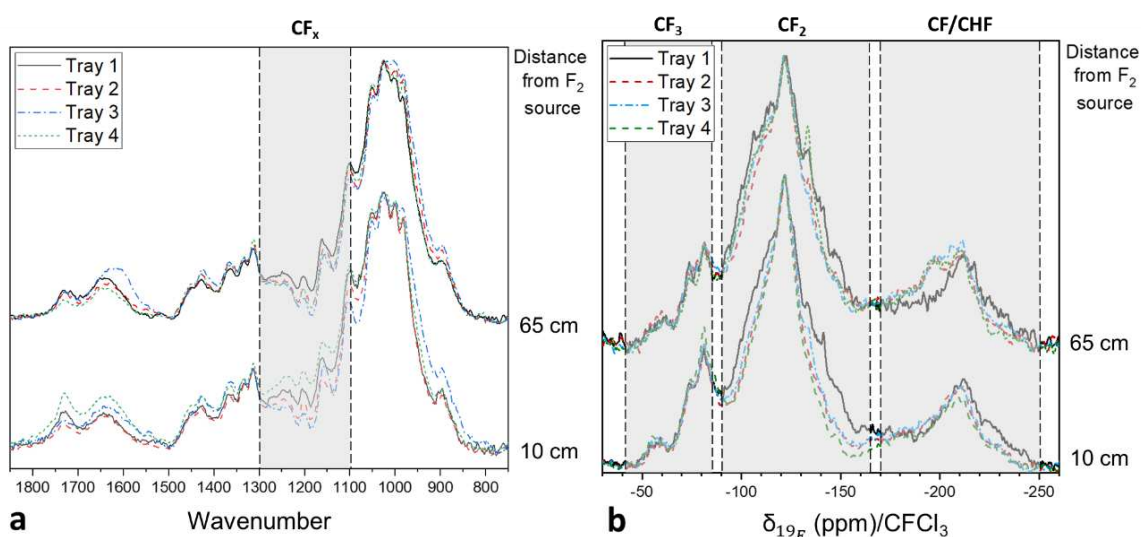


Figure 2: (a) IR and (b) ¹⁹F NMR spectra of fluorinated flax fibers

3.2 Modification of surface energy

When controlled, fluorination of flax fiber allows to modify the surface energy of the latter, by reducing its polar component (γ_s^p). In order to identify and quantify the modifications resulting from the treatment, wetting tests by tensiometric method were carried out.

Table 1 summarizes the evolution of polar (γ_s^p), dispersive (γ_s^d) and total (γ_s) surface energy of both pristine and fluorinated flax fibers. This treatment significantly lowered the polarity of fibers, from 19.1 ± 9 mN.m⁻¹ to 5.8 ± 2.4 mN.m⁻¹.

In addition, when considering the experimental uncertainties, it is evident that the fluorinated fibers are more homogeneous than the raw ones; vegetal fibers being natural materials, they present a disparity between them [17]. When it is well controlled, fluorination treatment allows this variability to be limited and a surface energy with a reduced data dispersion is obtained for treated fibers compared to the raw ones. From an industrial point of view, this appears as extremely promising.

On the contrary, we noticed that the dispersive component remains nearly constant after the fluorination treatment. Therefore, and knowing the fact that the dispersive constant is strongly related to the surface texture [18], the absence of changes may suggest the maintaining of the surface roughness during the fluorination treatment.

Table 1: Polar, dispersive and total surface energy of raw and fluorinated flax fibers

Sample	γ_s^p (mN/m)	γ_s^d (mN/m)	$\gamma_s^{\text{tot.}}$ (mN/m)
Raw	19.1 ± 9.0	22.5 ± 2.0	41.6 ± 11
Fluorinated	5.8 ± 2.4	21.1 ± 3.6	26.9 ± 6.0

3.2 Effect of fluorination treatment on mechanical properties of composite

Liotier *et al.* [1] have already demonstrated that, if the polar component of vegetal fibers fiber is reduced by a given treatment (thermal treatment in their case), the wettability of fibers by the polymer matrix will be improved and therefore, the overall mechanical behavior of composites manufactured is improved with treated fibers (even if fiber properties at rupture are reduced). This phenomenon was related to the improvement of the wettability of the fibers by the matrix, allowing to reduce the micro-porosity at the filler/matrix interface as already observed in the literature [3,12].

Thereby, in order to evaluate the impact of the flax fiber fluorination on the mechanical performance of eco-composite formed with this natural reinforcement, laminates plates of composites were manufactured with raw flax fibers reinforcement on one side and fluorinated flax fiber reinforcement on the other. The materials thus formed were then analyzed by flexural tests in the exactly same conditions in order to be compared. Results (Figure 3) evidenced a 25% increase of the Young's modulus (E) and a 10% increase of the maximal flexural stress (σ_m) whereas a 15% decrease of percentage of maximal elongation (A%) is observed. It is to note that the changes of these 3 values are achieved without overlapping the experimental uncertainty bars, demonstrating that the enhancements are significant. In addition, the improvements of E and σ_m while A% is decreased highlight a stiffening of the material thanks to the fluorination of its reinforcements (vegetal fibers).

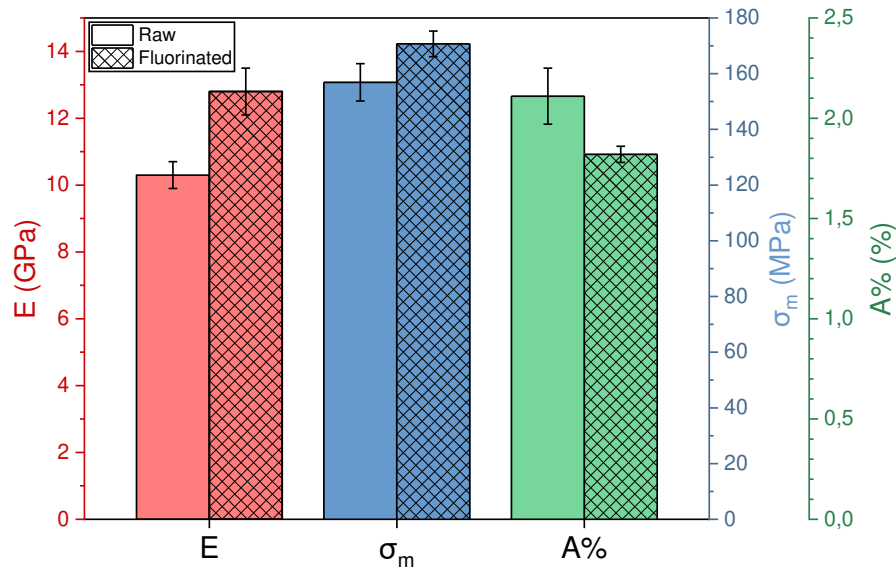


Figure 3: Flexural properties of composites made from raw and fluorinated flax fibers (E = Young's modulus; σ_m = Ultimate tensile strength; A% = percentage of maximal elongation)

4. Conclusion

The present work was focused on the effect of the fluorination treatment of flax fibers on the mechanical behavior of composites reinforced by fluorinated fibers. Fluorination has been realized at a large scale in a 50L reactor and have allowed to covalently graft fluorine atoms at the outmost surface of flax fibers. In addition, this treatment was carried out homogeneously over the 65cm length and the 4 trays of fibers introduced into the reactor and has allowed to reduce the fibers' polar component of surface energy. Thanks to this polarity decrease, the gap between the surface energies of the fibers and polymer matrix (Epoxy) was reduced; in other words, the wetting of the fiber by the polymer is improved during the infusion process (probably due to the fact that the porosity of the composite thus formed is significantly decreased). Therefore, mechanical performance of these composite is improved (a 25% increase of the Young's modulus (E) and a 10% increase of the maximal flexural stress (σ_m)), without any chemical coupling agent harmful to the environment or solvent for the chemical reaction.

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