

# Fluorination as an Effective Way to Reduce Natural Fibers Hydrophilicity

K. Charlet, F. Saulnier, D. Gautier, M. Pouzet, M. Dubois  
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**Abstract** In order to get composite materials with high mechanical properties, the quality of the interface between the fibres and the matrix has to be good enough to enable the load transfer. In the case of wood polymer composites, made of hydrophilic wood particles and of a generally non-polar polymer, the lack of natural compatibility between the constituents hinders the load transfer. Aiming at decreasing the gap of polarity between wood fibres and polymer matrices, fluorination has been applied to wood. This treatment is known to be very efficient to make more hydrophobic materials without requiring solvent or high temperature. After the optimization of the treatment parameters so as to get a high level of fluorine grafting without burning the particles, the hygroscopic and thermal behaviors of the fluorinated wood flour have been evaluated and compared to the non-treated flour. For that purpose, several analyses were carried out: FT-IR spectroscopy,  $^{19}\text{F}$  solid-state NMR spectroscopy, SEM, contact angle measurements, TGA. The fluorine based treatment was shown to decrease notably the capacity of the wood particles to absorb water without damaging their surfaces. Lastly, at the composite scale, the wood fluorination was shown to strongly reduce its hydrophilicity and to largely enhance its tensile and flexural properties. This is directly linked with the improvement of the compatibility between the treated (and thus, less hydrophilic) wood particles and the polymer matrix, as also proved by X-ray tomography.

**Keywords** Wood · Fluorination · Composite · Hydrophilicity

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## Introduction

Wood fibres, among other natural fibres, are increasingly used in replacement of usual aramid, carbon or glass reinforcements in composites, in order to reduce the amount of fossil carbon produced every day. The most common application fields of wood polymer composites are building, automotive, furniture and packaging industries. These composites give added value to a relatively abundant and cheap raw material, i.e. co-products of wood transformation. Nevertheless, their use is restricted to non-structural applications because of the lack of compatibility between the hydrophilic wood reinforcements and the hydrophobic polymer matrix, which generates porosity and low ability to transfer load at the interface, leading to poor composite mechanical properties. Therefore, a pre-treatment of the wood reinforcements is often necessary before processing these composites. During the last few years, various treatments have been developed to decrease wood's hydrophilic character and make it more compatible with polymer matrices (Guyonnet 1999; Podgorski et al. 2000; Ichazo et al. 2001; Lu et al. 2005; Tserki et al. 2005; Karmarkar et al. 2007; Nachtigall et al. 2007; Dominkovics et al. 2007; Dányádi et al. 2010; Ayrilmis et al. 2011; Acda et al. 2012; Islam et al. 2012; Zhang 2014). However, none of them is really convincing at the industrial scale in the case of wood based composites since they are either environmentally harmful, hardly efficient, highly energy-consuming or very costly.

Since few years, direct fluorination has been used to treat the surface of polymers, in order to enhance their barrier property against multiatomic molecules, e.g. hydrocarbons, and improve their chemical resistance to solvent attack (Kharitonov et al. 2005; Kharitonov 2008). It is known to decrease the permeability of materials, mainly polymers. The application of direct fluorination to synthetic fibres, such as aramid fibres, was shown to have a clear impact on material surface energy (Maity et al. 2007). In particular, when applied to carbon fibres, direct fluorination led to a noticeable increase in fibre hydrophobicity (Bismarck et al. 1997; Dubois et al. 2005; Ho et al. 2007; Guérin et al. 2012). The application of direct fluorination to lignocellulosic products has been studied in the past with the intention of making Kraft paper waterproof (Sapieha et al. 1990). Then the surface fluorination of paper was developed using the  $\text{CF}_4$  radio-frequency plasma technique (Sahin et al. 2002). In both studies, the published results reported a significant increase in the paper contact angle (i.e. a decrease in the hydrophilic character) after fluorination.

These findings suggest that direct fluorination could be applied in the treatment of wood fibres used as reinforcements for polymer matrices. To the authors' best knowledge, the use of fluorine chemistry to enhance the properties of wood based composites has never been studied before. This work focuses on the direct fluorination of wood flour in order to reduce its hydrophilic character and then improve its compatibility with unsaturated polyester. Changes in the structure of the wood and the impact on its properties are observed and discussed, in order to verify the validity of this method to produce good quality composites. The main difficulty and, at the same time, the main advantage, is the high reactivity of molecular

fluorine F<sub>2</sub> towards wood. With such a reactive sample, fluorination, i.e. the formation of C–F covalent bonds, competes with wood decomposition; when the fluorination is not controlled the wood may react with fluorine gas to form volatile perfluorinated groups such as CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub>. In other words, the wood may burn in the fluorine atmosphere as it does in air at high temperature.

The first objective was therefore the perfect control of the fluorination conditions in order to treat only the surface of the wood. Once the fluorination parameters were optimised, both the non-treated and fluorinated wood flours were characterized by Fourier transform infrared (FT-IR) spectroscopy, <sup>19</sup>F solid-state nuclear magnetic resonance (<sup>19</sup>F NMR) spectroscopy, scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA), and hygroscopic analysis in order to highlight the effects of the treatment.

The second objective was to evaluate the influence of the wood flour treatment on the composite properties. Thus, after the composite processing, the amounts of pores within the treated and non-treated wood composites were revealed by X-ray tomography. Then, tensile and flexural tests were performed on unsaturated polyester reinforced with non-treated or fluorinated wood flours. Contact angle measurements were used to estimate the change in the composite surface energy due to fluorination. Finally, the effect of humidity was investigated by testing composites that had been stored several days at normal or high relative humidity.

## Materials and Methods

### *Materials*

The wood flour under study was a mix of spruce and Douglas species obtained from sawmill co-products in Auvergne, France. Its density was measured by the solvent method using xylene and toluene and was found equal to  $1.41 \pm 0.17$ . The flour was sifted so that its grading was smaller than 250  $\mu\text{m}$ . The polymer used to process the derived composites was unsaturated polyester Norsodyne G703, from Cray Valley, whose density was given equal to 1.17.

### *Direct Fluorination of the Wood Flour*

About 5 g of wood flour were placed on a tray in a nickel reactor. The gas inlet was located to the left of the sample. The sample was first outgassed under a dynamic vacuum ( $-960$  mbar) at 150 °C for 2 h in order to remove all traces of water. Actually, water molecules may be adsorbed on the surface of the wood flour and react with fluorine gas (pure F<sub>2</sub>) to form HF molecules, which may act as a catalyst for fluorination, leading to the inhomogeneity of the treatment. The reaction oven was divided into three parts: it was set at 42 °C on the left, 55 °C in the middle and

70 °C on the right. Such a temperature gradient is necessary to avoid a high fluorination rate near to the gas inlet of the oven. This variation allows the control of the fluorination process and leads to a homogenous treatment. A partial vacuum was applied to the closed reactor (−20 mbar) and F<sub>2</sub> gas was injected in addition to N<sub>2</sub> gas to reach 1 atm. The total pressure inside the closed reactor was maintained constant for 3 h, and five additions of fluorine were performed in order to compensate for the consumption of molecular fluorine during the reaction. Finally, after 2 h under a flow of N<sub>2</sub> gas at 150 °C to remove all the F<sub>2</sub> molecules, and cooling to ambient temperature for 11 h, the flour was heated again to 150 °C with a flow of N<sub>2</sub> gas for 1 h to eliminate traces of adsorbed F<sub>2</sub>, HF, CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> molecules.

### ***FT-IR and NMR Spectroscopy***

Samples of fluorinated wood flour were taken at different locations in the reactor in order to check the homogeneity of the treatment using FT-IR and <sup>19</sup>F NMR analyses. FT-IR spectroscopy was performed in attenuated total reflectance (ATR) mode using a SHIMADZU FT-IR 8300 spectrometer. The spectra were recorded in the mid infrared region (4000–400 cm<sup>−1</sup>), and 64 co-added scans were collected for each sample. <sup>19</sup>F NMR experiments were carried out using a Bruker Avance spectrometer, with working frequencies of 282.2 MHz. For magic angle spinning (MAS), a Bruker probe operating with 2.5 mm rotors was used. A simple sequence was performed with a single  $\pi/2$  pulse length of 4.0  $\mu$ s. 128 scans were recorded. The MAS spinning speed was set to 34 kHz, high enough to significantly average and weaken the <sup>19</sup>F–<sup>19</sup>F homonuclear coupling, which is the main interaction. <sup>19</sup>F chemical shifts were externally referenced to CFCI<sub>3</sub>.

### ***TGA***

The thermogravimetric analysis was performed under a nitrogen atmosphere of 0.9 bars using a PerkinElmer TGA 4000 analyser. About 10 mg of wood flour was heated from 35 to 450 °C with a heating rate of 5 °C/min. Then the sample was cooled to 35 °C with a cooling rate of 50 °C/min.

### ***SEM Analysis***

The surface morphology of the wood particles before and after fluorination was observed by SEM analysis, performed with a Phenom FEI microscope.

## *X-ray Tomography*

Wood polyester composites were analyzed by X-ray tomography in order to determine the amount of pores present within the volume of the sample and to compare these amounts according to the applied treatment. The device used, a compact SkyScan 1174, enables the 3D reconstruction of the composite with a resolution of 30  $\mu\text{m}$  under 50 kV, which means that the micro-porosity cannot be visualized. Therefore, this may give an idea of the potential improvement of the fibre/matrix compatibility. The dimensions of the observed composites were 10 mm  $\times$  10 mm  $\times$  1.76 mm.

## *Hygroscopic Testing of the Wood Flour*

Humidity-controlled chambers were created following the NF EN ISO 483 standard, so as to study the hygroscopic behaviour of the wood flour under different relative humidity (RH) conditions (9, 33, 59, 75 and 98 % RH). Hermetic jars were filled with diverse saturated salt solutions, which are listed in Table 1. A plastic tube and an iron grid were used to maintain the sample 3 cm above the solution and thus prevent direct contact with water. The wood flour was placed in plastic caps and dried in an oven at 90  $^{\circ}\text{C}$  for 48 h to attain the anhydrous state. Then each sample was conditioned in the humidity-controlled chambers until its weight was stabilized.

Hygroscopic characterization was carried out by measuring the weight variation of the wood samples throughout the conditioning procedure for each relative humidity. Finally, the water content of the wood was evaluated using the following formula, where  $m$  is the sample weight at the considered time and  $m_0$  the weight at the anhydrous state:

$$x(t) = (m(t) - m_0)/m_0 \quad (1)$$

For each relative humidity value, five samples of non-treated and fluorinated wood flour were analysed.

**Table 1** Saturated salt solutions and corresponding relative humidity at 20  $^{\circ}\text{C}$

Saturated aqueous salt solutions	RH (%)
Potassium hydroxide	9
Magnesium chloride hexahydrate	33
Sodium bromide	59
Sodium chloride	75
Potassium sulphate	98

## *Wood-Polyester Composite Processing*

Wood polyester composites with a reinforcement weight fraction of 45 % (corresponding to a volume fraction of 40 %) were processed by hot compression molding, using a SATIM hot press. The wood polyester mixture was poured into an aluminium mold of 100 mm × 100 mm × 2 mm covered with 0.12 mm thick PTFE sheets on each internal face (aimed at easing the final demolding). Then, the closed mold was placed in the press and kept under a pressure of 60 kN and a temperature of 80 °C for 2 h, so as to ensure the resin cross-linking. The cooling to ambient temperature was performed using air under pressure. Treated and non-treated wood flour composites were processed in exactly the same way, without any pre-curing of the materials. Samples for the mechanical tests were taken from the plates thus obtained; their width was 10 mm and their thickness was 1.76 mm.

## *Composite Mechanical Characterization*

**Tensile tests** The tensile tests were performed on a Zwick/Roell Zmart Pro test machine, with a prescribed crosshead displacement rate of 1 mm/min and a gage length of 50 mm, until the rupture of the sample. The initial length of the samples was 70 mm, adapted from the standard NF EN ISO 527-3. The tests were conducted at room temperature (about 23 °C) and relative humidity (about 40 %). The longitudinal stress ( $\sigma$ ) and strain ( $\varepsilon$ ) of the sample were calculated from the measured force ( $F$ ), the sample elongation ( $\Delta L$ ), the sample section  $S_0$  (supposed to be constant), and the gage length  $L_0$  as follows:

$$\sigma = F/S_0 \quad (2)$$

$$\varepsilon = \Delta L/L_0 \quad (3)$$

**Flexural tests** Three point bending tests were performed on an Instron 5543 test machine equipped with a 500 N load cell, at room temperature (about 23 °C) and relative humidity (about 40 %). The length of the sample was 35 mm and the distance between the supporting pins was set to 28 mm, following the standard NF EN ISO 178. The samples were tested at a crosshead displacement rate of 1 mm/min with the load applied at mid-span. The flexural strain ( $\varepsilon$ ) and stress ( $\sigma$ ) at the middle of the sample were calculated from the deflection ( $Y$ , corresponding to the crosshead displacement) and the force ( $F$ ). Considering the material as homogeneous, we had:

$$\varepsilon = 6hY/L_0^2 \quad (4)$$

$$\sigma = 3FL_0/2bh^2 \quad (5)$$

where  $L_0$  is the span,  $b$  and  $h$  respectively the width and the thickness of the samples.

### *Hygroscopic Behavior of the Composites*

**Contact angle measurements** Contact angle measurements were carried out on an Easy Drop Krüss device. A water microdroplet of 5  $\mu\text{L}$  was deposited on the composite surface. Once the droplet was stabilized, the picture was frozen and analysed using the Krüss DSA software that evaluates directly the contact angle. For each composite, five microdroplets were deposited and an average contact angle was calculated.

**Composite water absorption** After curing 24 h at 80  $^\circ\text{C}$  to remove water, 35 mm long composite samples were stored in a climatic chamber at a constant relative humidity (80 %) and a constant temperature (20  $^\circ\text{C}$ ). The weight of the samples (4 of each type of composites) was measured every day at the same moment of the day until equilibrium. Then, the water content of the sample was estimated as:

$$W(t) = (m(t) - m_0)/m_0 \quad (6)$$

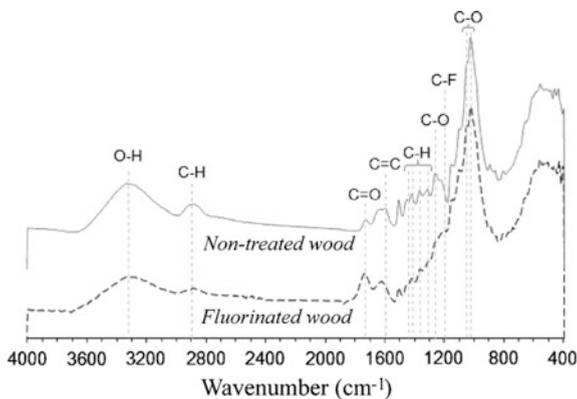
with  $m(t)$  the mass of the moist sample at time  $t$  at equilibrium and  $m_0$  its dry mass. After 18 days, their weight being almost constant, the samples were rapidly tested to get their flexural properties, following the same protocol as described in section '[Composite Mechanical Characterization](#)'. At the time of the tests, the ambient temperature was 21  $^\circ\text{C}$  and the relative humidity 44 %.

## **Results and Discussion**

### *Covalent Grafting of Fluorine on Wood*

The ATR FT-IR spectra of the wood flour before and after direct fluorination are given in Fig. 1. The absorbance peaks in the non-treated wood flour spectrum correspond to the main bonds of the wood components (Müller et al. 2003; Popescu et al. 2013; Schwanninger et al. 2004). The broad peak around 3320  $\text{cm}^{-1}$  is due to the  $-\text{OH}$  hydroxyl groups in cellulose whereas the peak around 2900  $\text{cm}^{-1}$  is ascribed to the asymmetric and symmetric mode of hydrocarbon (C-H) stretching. The C=O stretching vibration of carbonyl, carboxyl and acetyl groups appears at 1740  $\text{cm}^{-1}$ . The band at 1640  $\text{cm}^{-1}$  is due to C=O stretch of aromatic ketones. The band at 1600  $\text{cm}^{-1}$  corresponds to the C=C stretching of aromatic skeletal in lignin.

**Fig. 1** FT-IR spectra of wood flours



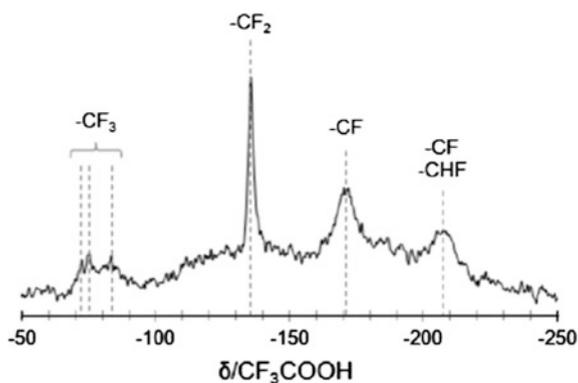
C–O stretching in lignin is observed at  $1260\text{ cm}^{-1}$  and the large peak at  $1020\text{ cm}^{-1}$  is attributed to C–O stretching vibration.

It is well known that wood hydrophilicity is essentially due to the hydroxyl groups (–OH) of both the cellulose and hemicelluloses. Indeed, these hydroxyl groups have the property of absorbing water molecules, forming hydrogen bonds. The FT-IR spectroscopy analysis of fluorinated wood flour reveals a significant decrease in the number of hydroxyl bonds ( $3320\text{ cm}^{-1}$ ). As there are fewer sites for hydrogen bonding, the fluorinated wood particles should adsorb less water. In other words, the decrease in the number of –OH groups in the wood flour was one of the first proofs of the weakening of its hydrophilicity.

Fluorination also induces the substitution of certain specific atoms in the treated material by fluorine atoms. Hydrogen atoms in hydrocarbon groups on the wood surface are expected to be replaced by fluorine, because of both the weakness of C–H bonds and the reactivity of molecular fluorine. In fact, the substitution of C–H bonds ( $2900\text{ cm}^{-1}$ ) by carbon-fluorine (C–F) bonds ( $1180\text{ cm}^{-1}$ ) was observed after the fluorination of the wood flour. This latter band corresponds to covalent C–F bonds (Kharitonov 2008). Even with weak intensity, its presence underlines the formation of C–F bonds onto the wood components. Moreover, the fact that samples taken at various distances from the gas inlet of the reactor showed similar spectra confirms that the temperature gradient ensured the homogeneity of the fluorine grafting onto the wood.

The  $^{19}\text{F}$  NMR measurements were used to confirm both the covalent grafting of fluorine atoms and the nature of the fluorinated groups, i.e. –CF, –CF<sub>2</sub> or –CF<sub>3</sub> (Isbester et al. 1997; Aimi et al. 2004; Zhang et al. 2010). An example of the  $^{19}\text{F}$  MAS NMR spectrum of fluorinated wood flour is presented in Fig. 2. It is typical of the samples, whatever their location in the reactor. The resonances are attributable to the different groups, namely –CF, –CF<sub>2</sub> or –CF<sub>3</sub>. The broad signal at  $-135\text{ ppm}$  versus  $\text{CFCl}_3$  matches –CF<sub>2</sub> groups, while the signal at  $-182\text{ ppm}$  corresponds to C–F bonds and the signals at  $-74$  and  $-83\text{ ppm}$  are both attributed to –CF<sub>3</sub> groups with different neighbours. Finally, the signal at  $-207\text{ ppm}$  is due to an aromatic –CF bond or –CHF bond. Bearing out the evidence of IR spectroscopy, NMR

**Fig. 2**  $^{19}\text{F}$  NMR spectrum of fluorinated wood flour



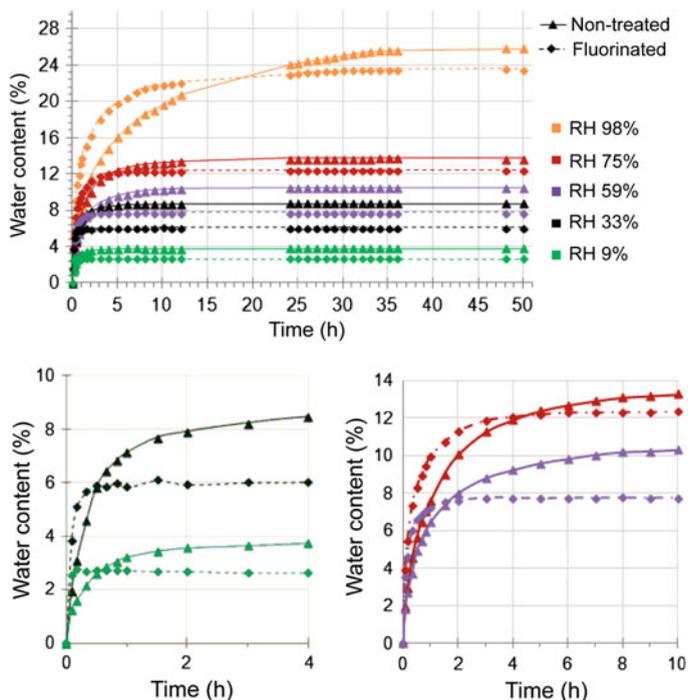
unambiguously highlights the presence of both fluorinated and perfluorinated groups on the wood surface.

The electronegativity of the fluorine atom, the highest in the periodic table, confers a strong polarity to the carbon-fluorine bonds, which creates a polar hydrophobicity of the fluorinated compounds. For this reason, the presence of fluorine atoms on the wood surface should imply a decrease in the hydrophilic character of the resulting samples. This decrease has to be confirmed by hygroscopic characterisation.

### *Decrease of Wood Hydrophilicity*

Through the adsorption effect, the water content of the wood moves towards an equilibrium state according to the ambient relative humidity. Thus, when the wood flour was conditioned in a humidity-controlled chamber after drying, the water content increased to match the conditions of the enclosure. Continuous measurements of the sample weight allowed the evolution of the water content for each relative humidity value to be monitored, from the anhydrous state to the equilibrium point. The adsorption curves of untreated and fluorinated wood flours are given in Fig. 3. The hygroscopic analysis of the non-treated wood flour was performed both to validate the method and to make a reference to check the effect of direct fluorination on the hygroscopic behaviour of wood flour. The experimental results corresponded with previous studies found in the literature in terms of water content (Stamm et al. 1964). For example, the water content of wood after equilibrium is known to be about 11 % for a relative humidity of 60 % at 20 °C, and the wood flour studied here contained 10.5 % of water under 59 % relative humidity at the same temperature.

After fluorination, an increase in the adsorption rate was observed. For instance, in the case of a relative humidity equal to 75 %, the water content of fluorinated wood flour was stabilized in 5 h, compared to 24 h for the non-treated wood flour.



**Fig. 3** Adsorption curves of the wood flour before and after fluorination for various relative humidity conditions (*top* global curves; *bottom* zoom on short times)

Hygroscopic analysis also underlined the decrease in the equilibrium water content of the wood flour after fluorination. The water content of both non-treated and fluorinated wood flours under the different relative humidity conditions are listed in Table 2. An average decrease of 2 points in the water content of the wood flour after treatment can be observed, representing a drop of 10–30 % in the water content.

This analysis shows that direct fluorination efficiently lowers the water content in wood flour. This decrease can be explained by the reduction in the number of sites for hydrogen bonding. In addition, the fluorinated wood flour reaches its water

**Table 2** Water content of the wood flours under various humidity conditions

Relative humidity (%)	Water content in the non-treated wood (%)	Water content in the fluorinated wood (%)	Loss of water content (%)
9	3.7 ± 0.2	2.7 ± 0.3	30
33	8.7 ± 0.3	6.1 ± 0.5	30
59	10.5 ± 0.4	7.8 ± 0.2	26
75	13.8 ± 0.3	12.4 ± 0.2	10
98	25.8 ± 0.8	23.6 ± 0.2	9

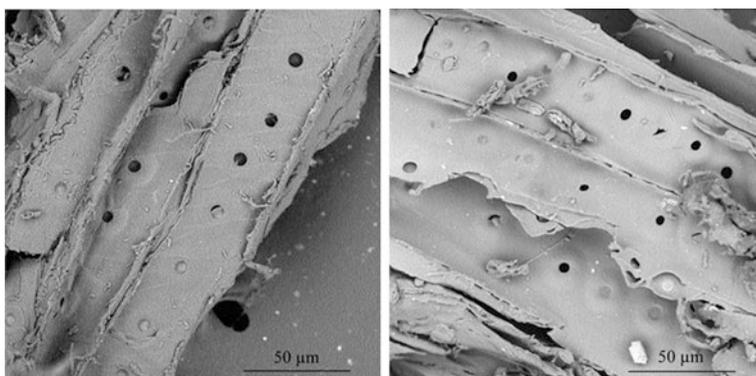
equilibrium point faster than the non-treated wood flour. The presence of electronegative fluorine in the constitution of the fluorinated wood increases the attractiveness of its surface and accelerates its reaction with water.

### ***Preservation of the Structure of Wood***

Excessive fluorination may cause important damage to a material surface because of the formation of volatile species such as  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ . In order to verify that the treatment does not damage the wood texture, a SEM analysis was performed. Examples of micrographs of wood particles (with or without fluorination) are given in Fig. 4. The tracheid physical structure appears preserved after direct fluorination; even the wood pits were maintained intact.

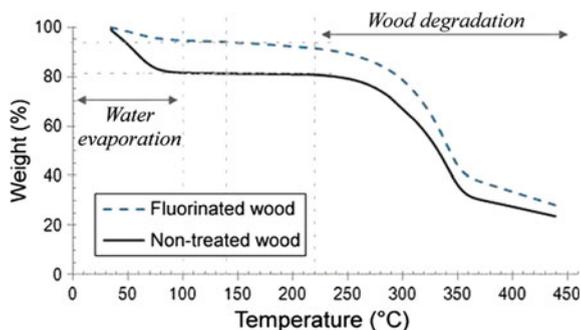
### ***Analysis of the Thermal Behavior of Wood***

TGA was performed on raw and fluorinated wood flours. The curves obtained are presented in Fig. 5. The first weight loss in the curves corresponds to water desorption, which occurred before  $100\text{ }^\circ\text{C}$  due to the pressure and the  $\text{N}_2$  atmosphere. The weight loss for the fluorinated sample between  $140$  and  $220\text{ }^\circ\text{C}$  is due to the decomposition of carbon-fluorine bonds. It corresponds to about 5 % of the sample weight. Wood degradation was noticed from  $220\text{ }^\circ\text{C}$ , in agreement with recent studies on wood thermal degradation (Jeske et al. 2012; Poletto et al. 2012). The TGA data underline that the treatment is effective up to  $140\text{ }^\circ\text{C}$ . Since the unsaturated polyester resin is usually polymerized at  $80\text{ }^\circ\text{C}$ , the direct fluorination of wood flour appears to be an efficient treatment for wood flour used as a polyester composite reinforcement.



**Fig. 4** SEM micrographs of an untreated (*left*) or a fluorinated (*right*) wood particle

**Fig. 5** TGA curves of wood flours



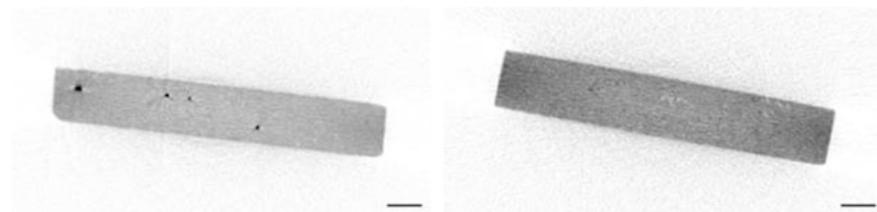
### *Improvement of the Composite Health*

X-ray tomography enabled us to see inside the composite samples. Due to the negligible differences in densities between wood (about 1.4) and polyester (about 1.2), the particles were not visible. Nevertheless, we managed to distinguish the pores, which are air bubbles entangled in the composite during its processing. Figure 6 shows examples of scans obtained for the two kinds of composites.

The difference between the two composites made with non-treated wood or with fluorinated wood is obvious: the latter exhibited much fewer pores than the former. Since the composites were processed in exactly the same way, this observation can only be attributed to the fluorination. It may enhance the compatibility between wood particles and polyester, allowing less volume to be available for air and hindering the formation of bubbles when the counter mold is pressed onto the materials. This tends to prove that the composite's quality is improved by the pre-treatment of the wood. Better properties are thus expected from the fluorinated wood composite.

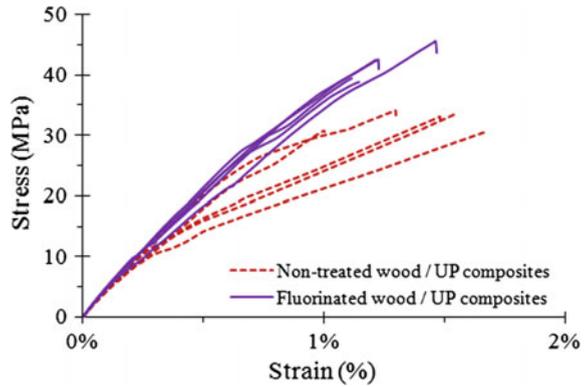
### *Improvement of the Composite Mechanical Properties*

The tensile stress-strain curves of the composites with non-treated and fluorinated wood flours are given in the Fig. 7 and Table 3. A slight increase in the composite



**Fig. 6** X-ray tomography images of the cross-sections of two composites made of non-treated (*left*) or fluorinated (*right*) wood flours (scale bars = 1 mm)

**Fig. 7** Tensile stress-strain curves of composites with non-treated or fluorinated wood flours



**Table 3** Tensile properties of the composites with non-treated or fluorinated wood flours

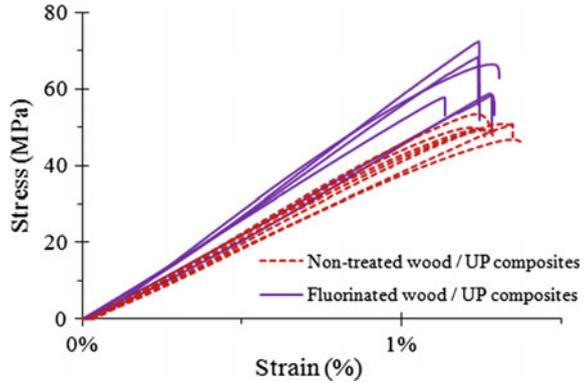
Composites	E (GPa)	$\sigma_R$ (MPa)	$A_R$ (%)
Non-treated wood/UP	$4.4 \pm 0.2$	$32.4 \pm 1.5$	$1.4 \pm 0.3$
Fluorinated wood/UP	$4.8 \pm 0.2$	$41.7 \pm 2.4$	$1.3 \pm 0.1$

stiffness (E) was observed with the direct fluorination of the reinforcements (+8 %), as shown in the higher initial slope of the curve. The mean tensile strength ( $\sigma_R$ ) was also improved by the treatment (+29 %). Nevertheless, the elongation at break ( $A_R$ ) was slightly decreased (-6 %) but this reduction is negligible due to the high standard deviations observed for this property (10–20 %).

We can deduce from the enhancement of the tensile properties that the fibre/matrix interface is of better quality when the wood flour has been previously fluorinated. Compared with other treatments, the direct fluorination developed here enables an improvement of the composite tensile properties comparable to treatments using maleic anhydride or silane. Actually, wood-polypropylene composites showed increases in their elastic modulus of about 6 % and in their tensile strength of maximum 20 % after a maleic anhydride treatment (Garcia et al. 2005), whereas the addition of 1 wt% of silane to a 30 wt% wood reinforced polypropylene improved the composite tensile strength by 12 % (Nachtigall et al. 2007).

The effect of the fluorination on the flexural mechanical properties of the composites was also studied. The stress-strain curves obtained for both types of composites are presented in Fig. 8 and the corresponding mean values are given in Table 4. As for the tensile tests, the composites appeared to be stiffer after the direct fluorination of the reinforcements (+25 %). For both types of composite, failure occurred for similar values of strain. The strength was also increased by the wood treatment (+27 %). Compared with the data available in the literature on the effect of other treatments on the composite flexural properties, fluorination appears as the most efficient. Actually, the addition of 4 % of bamboo charcoal to wood polymer composites was found to increase strength to a similar level (+32 %) but the

**Fig. 8** Flexural stress-strain curves of composites with non-treated or fluorinated wood flours



**Table 4** Flexural properties of the composites with non-treated or fluorinated wood flours

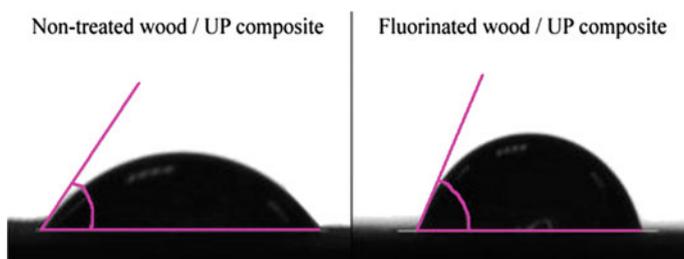
Composites	E (GPa)	$\sigma_R$ (MPa)	$A_R$ (%)
Non-treated wood/UP	$4.5 \pm 0.3$	$50.1 \pm 1.8$	$1.4 \pm 0.1$
Fluorinated wood/UP	$5.6 \pm 0.6$	$63.8 \pm 5.7$	$1.3 \pm 0.1$

increase in the flexural modulus was relatively low (+9 %) (Li et al. 2014). Also, an alkali treatment applied on different tropical wood polymer composites improved the strength of up to 16 % and the modulus of 13 % maximum (Islam et al. 2012).

To conclude on this part, the fluorination of the wood flour tends to improve both flexural and tensile stiffness and strength of the derived composites, which could be explained by a better load transfer due to an improvement in the compatibility between the wood reinforcements and the polyester resin. This is in agreement with the decrease of the amount of pores after the wood treatment, as presented in section ‘Improvement of the Composite Health’.

### *Improvement of the Composite Hygroscopic Behavior*

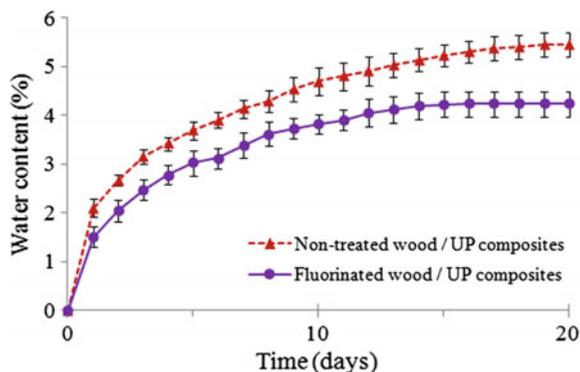
**Decrease of the composite surface energy** An overview of the pictures obtained for the measurement of contact angles between water and the wood polymer composite surfaces is given in Fig. 9. It is to be noted that these images were taken when the droplets were stabilized. The contact angle increases with the treatment of the wood reinforcements by about 10 %, from  $75.9^\circ \pm 13.1^\circ$  to  $83.6^\circ \pm 8.6^\circ$ . The relatively large standard deviations can be explained by the presence of random surface micropores influencing the measurements. Despite this scattering of data, the fluorination of wood flour is likely to enhance the surface properties of the composite against water.



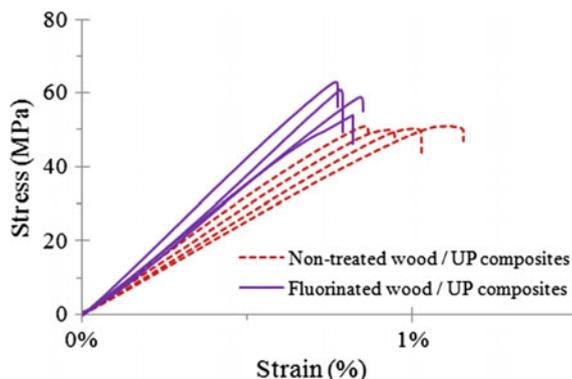
**Fig. 9** Examples of contact angle images for the non-treated (*left*) or fluorinated (*right*) wood composites

**Decrease in the composite water absorption** The composites that were stored under a constant and relatively high humidity (80 %) at 20 °C were weighed every day until their weight stabilized. The results of these measurements are given in Fig. 10. It appears first that the fluorinated wood composite exhibits a lower water content at the hygroscopic equilibrium (4.2 %) compared with the non-treated wood composite (5.5 %), which means that the former absorbs less water than the latter. This is in agreement with the values found for the fluorinated wood flour itself which, after storage under a relative humidity of 85 %, presented a water content about 30 % below the one of non-treated wood flour (Saulnier et al. 2013). This drop of water content (−23 %) has already been observed for immersed silane- or MAPP-treated wood composites, but at a lower level (−10 and −15 % respectively) (Ichazo et al. 2001). Also, it was reported that the addition of 4 % of bamboo charcoal in a wood polymer composite decreased the equilibrium water content of 6 % (Li et al. 2014). Benzylation was proved to be very efficient to reduce the composite water uptake but at the expense of its mechanical properties (Dányádi et al. 2010). Secondly, this equilibrium is reached faster in the case of treated wood (14 days as against 16 days). Yet again, this follows the tendency of the fluorinated wood flour which, after storage at a relative humidity of 75 %, reached weight

**Fig. 10** Evolution of the water content of fluorinated or non-treated wood composites



**Fig. 11** Flexural stress-strain curves of composites stored 20 days under a relative humidity of 80 %



**Table 5** Flexural properties of the composites stored 20 days under a relative humidity of 80 %

Composites	E (GPa)	$\sigma_R$ (MPa)	$A_R$ (%)
Non-treated wood/UP	$5.8 \pm 0.5$	$50.6 \pm 0.4$	$1.0 \pm 0.1$
Fluorinated wood/UP	$7.8 \pm 0.6$	$59.2 \pm 3.4$	$0.8 \pm 0.1$

stabilization after 5 h, whereas the non-treated wood flour required 24 h (Saulnier et al. 2013).

#### Improvement of the composite mechanical behaviour in humid conditions

After a 20 day-storage under a relative humidity of 80 % and a constant temperature of 20 °C, wood polymer composites were tested to get their flexural properties. The obtained curves are shown in Fig. 11 and the corresponding values are presented in Table 5.

It can be noticed that the moduli of these samples are higher than those obtained under ambient conditions. This may be explained by the fact that the composites were not cured after processing and that humidity may have acted as an ageing agent that completed the reticulation of the polyester matrix during the storage at 80 % RH [this phenomenon has already been underlined in some studies on thermoset resins (Stamatakis et al. 2010; Odegard et al. 2011)]. Moreover, as in the case of ambient tests, fluorination increases the flexural properties of wood polymer composites. This tends to prove that, even after exposure to water, the fluorinated wood/UP composites keep good flexural properties.

## Conclusions

A decrease in the hydrophilic character of wood flour was obtained by direct fluorination using molecular fluorine  $F_2$ . This can be explained by the formation of C–F bonds onto the surface of the wood flour particles and the decrease in the

number of –OH groups on the wood, observed using FT-IR and  $^{19}\text{F}$  RMN spectroscopy, and confirmed by hygroscopic characterisation. Moreover, SEM analysis showed that the treatment did not damage the physical structure of the wood. The thermal behaviour of wood flour remained stable under 100 °C after direct fluorination, which enables its use as a reinforcement for unsaturated polyester or other resins with low-temperature manufacturing characteristics.

An improvement of the tensile and flexural properties of the wood-polyester composite was obtained by the direct fluorination of the reinforcements. This can be explained by better adhesion between polyester and wood after the treatment, leading to fewer pores as shown by X-ray tomography. The composite surface energy and its capacity to absorb water were also reduced after fluorination of the reinforcements. Large scale production of low-cost fluorinated wood flour may be proceeded at low temperature (i.e. with low energy cost) and with high reaction yield because of the intrinsic reactivity of the raw materials. Additional experiments are currently being carried out to decrease even further the hydrophilicity of the composites by applying fluorination to fluorinated wood flour composites.

## References

- Guyonnet, R., inventor; Wood curing method. US patent 5901463, 1999 May 11.
- Podgorski, L.; Chevet, B.; Onic, L.; Merlin, A.; Modification of wood wettability by plasma and corona treatments. *Int J Adhes Adhes*, 2000, 20, 103-111.
- Ichazo, M.N.; Albano, C.; González, J.; Perera, R.; Polypropylene/wood flour composites: treatments and properties. *Compos Struct*, 2001, 54, 207-214.
- Lu, J.Z.; Wu, Q.; Negulescu, I.I.; Wood-fiber/high-density-polyethylene composites: Coupling agent performance. *J Appl Polym Sci*, 2005, 96, 93-102.
- Tserki, V.; Zafeiropoulos, N.E.; Simon, F.; Panayiotou, C.; A study of the effect of acetylation and propionylation surface treatments on natural fibres. *Comp Part A*, 2005, 36, 1110-1118.
- Karmarkar, A.; Chauhan, S.S.; Modak, J.M.; Chanda, M.; Mechanical properties of wood-fiber reinforced polypropylene composites: Effect of a novel compatibilizer with isocyanate functional group. *Comp Part A*, 2007, 38, 227-233.
- Nachtigall, S.M.B.; Cerveira, G.S.; Rosa, S.M.L.; New polymeric-coupling agent for polypropylene/wood-flour composites. *Polym Test*, 2007, 26, 619-628.
- Dominkovics, Z.; Dányádi, L.; Pukánszky, B.; Surface modification of wood flour and its effect on the properties of PP/wood composites. *Comp Part A*, 2007, 38, 1893-1901.
- Dányádi, L.; Móczó, J.; Pukánszky, B.; Effect of various surface modifications of wood flour on the properties of PP/wood composites. *Comp Part A*, 2010, 41, 199-206.
- Ayrlimis, N.; Jarusombuti, S.; Fueangvivat, V.; Bauchongkol, P.; Effect of thermal-treatment of wood fibres on properties of flat-pressed wood plastic composites. *Polym Degrad Stabil*, 2011, 96, 818-822.
- Acda, M.N.; Devera, E.E.; Cabangon, R.J.; Ramos, H.J.; Effects of plasma modification on adhesion properties of wood. *Int J Adhes Adhes*, 2012, 32, 70-75.
- Islam, M.S.; Hamdan, S.; Jusoh, I.; Rahman, M.R. *et al.*; The effect of alkali pretreatment on mechanical and morphological properties of tropical wood polymer composites. *Mater Design*, 2012, 33, 419-424.

- Zhang, H.; Effect of a novel coupling agent, alkyl ketene dimer, on the mechanical properties of wood-plastic composites. *Mater Design*, 2014, 59, 130-134.
- Kharitonov, A.P.; Taege, R.; Ferrier, G.; Teplyakov, V.V. *et al.*; Direct fluorination-useful tool to enhance commercial properties of polymer articles. *J Fluor Chem*, 2005, 126, 251-263.
- Kharitonov, A.P.; Direct Fluorination of Polymers. New York: Nova Publishers, 2008.
- Maity, J.; Jacob, C.; Das, C.K.; Kharitonov, A.P. *et al.*; Fluorinated aramid fiber reinforced polypropylene composites and their characterization. *Polym Composite*, 2007, 28, 462-469.
- Bismarck, A.; Tahhan, R.; Springer, J.; Schulz, A. *et al.*; Influence of fluorination on the properties of carbon fibres. *J Fluor Chem*, 1997, 84, 127-134.
- Dubois, M.; Guérin, K.; Giraudet, J.; Pilichowski, J.F. *et al.*; Direct fluorination of poly (p-phenylene). *Polymer*, 2005, 46, 6736-6745.
- Ho, K.K.C.; Beamson, G.; Shia, G.; Polyakova, N.V. *et al.*; Surface and bulk properties of severely fluorinated carbon fibres. *J Fluor Chem*, 2007, 128, 1359-1368.
- Guérin, K.; Dubois, M.; Houdayer, A.; Hamwi, A.; Applicative performances of fluorinated carbons through fluorination routes: a review. *J Fluor Chem*, 2012, 134, 11-17.
- Sapieha, S.; Verreault, M.; Klemberg-Sapieha, J.E.; Sacher, E. *et al.*; XRay photoelectron study of the plasma fluorination of lignocellulose. *Appl Surf Sci*, 1990, 44, 165-169.
- Sahin, H.T.; Manolache, S.; Young, R.A.; Denes, F.; Surface fluorination of paper in CF<sub>4</sub>-RF plasma environments. *Cellulose*, 2002, 9, 171-181.
- Müller, U.; Rätzsch, M.; Schwanninger, M.; Steiner, M. *et al.*; Yellowing and IR changes of spruce wood as result of UV-irradiation. *J Photoch Photobio B*, 2003, 69, 97-105.
- Popescu, M.C.; Froidevaux, J.; Navi, P.; Popescu, C.M.; Structural modifications of *Tilia cordata* wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy. *J Mol Struct*, 2013, 1033, 176-186.
- [25] Schwanninger, M.; Rodrigues, J.C.; Pereira, H.; Hinterstoisser, B.; Effects of shorttime vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib Spectrosc*, 2004, 36, 23-40.
- Isbester, P.K.; Kestner, T.A.; Munson, E.J.; High-resolution variable-temperature MAS <sup>19</sup>F NMR spectroscopy of fluorocarbon polymers. *Macromolecules*, 1997, 30, 2800-2801.
- Aimi, K.; Ando, S.; Conformation analysis and molecular mobility of ethylene and tetrafluoroethylene copolymer using solid-state <sup>19</sup>F MAS and 1H → <sup>19</sup>F CP/MAS NMR spectroscopy. *Magn Reson Chem*, 2004, 42, 577-588.
- Zhang, W.; Dubois, M.; Guérin, K.; Bonnet, P. *et al.*; Effect of curvature on C-F bonding in fluorinated carbons: from fullerene and derivatives to graphite. *Phys Chem Chem Phys*, 2010, 12, 1388-1398.
- Stamm, A.J.; Wood and cellulose science. New York: Ronald press, 1964.
- Jeske, H.; Schirp, A.; Cornelius, F.; Development of a thermogravimetric analysis (TGA) method for quantitative analysis of wood flour and polypropylene in wood plastic composites (WPC). *Thermochim Acta*, 2012, 543, 165-171.
- Poletto, M.; Zattera, A.J.; Forte, M.M.C.; Santana, R.M.C.; Thermal decomposition of wood: influence of wood components and cellulose crystallite size. *Bioresource Technol*, 2012, 109, 148-153.
- García, R.A.; Amélioration de la stabilité dimensionnelle des panneaux de fibres de bois MDF par traitements physico-chimiques. PhD thesis. Université de Laval, Québec, 2005.
- Li, X.; Lei, B.; Lin, Z.; Huang, L. *et al.*; The utilization of bamboo charcoal enhances wood plastic composites with excellent mechanical and thermal properties. *Mater Design*, 2014, 53, 419-424.
- Saulnier, F.; Influence de traitements physico-chimiques des renforts sur le comportement mécanique des composites à base de co-produits de bois. PhD thesis. Université Blaise Pascal, France, 2013.
- Saulnier, F.; Dubois, M.; Charlet, K.; Frezet, L. *et al.*; Direct fluorination applied to wood flour used as reinforcement for polymers. *Carbohydr Polym*, 2013, 94, 642-646.

- Stamatakis, G.; Knuutinen, U.; Laitinen, K.; Spyros, A.; Analysis and ageing of unsaturated polyester resins in contemporary art installations by NMR spectroscopy. *Anal Bioanal Chem*, 2010, 398, 3203-3214.
- Odegard, G.M.; Bandyopadhyay, A.; Physical aging of epoxy polymers and their composites. *J Pol Sci Pol Phys*, 2011, 49, 1695-1716.