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A NEW TREATMENT TO REDUCE WOOD HYDROPHILICITY

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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 and polar 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 waterproof Kraft paper and more hydrophobic carbon fibres, without using solvent or high temperature. The first step of this study was to optimize the treatment parameters (time, temperature, atmosphere…) so as to get a high level of fluorine grafting without damaging the particle surface. Several analyses were carried out to determine them (Fourier transform infrared spectroscopy, ^{19}F solid-state nuclear magnetic resonance spectroscopy, scanning electron microscopy…). Then, the hygroscopic and thermal behaviours of the fluorinated wood flour have been evaluated and compared to the non-treated wood flour, using for example contact angle measurements and thermogravimetric analysis. The fluorine based treatment was shown to decrease notably the capacity of the wood particles to absorb water without damaging their surfaces. Lastly, the mechanical and hygroscopic properties of the composites made with fluorinated wood and polyester matrix were determined. The results revealed that the wood fluorination strongly reduced the hydrophilicity of the composite, and largely enhanced 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:
Fluorination; wood; composite; hydrophilicity

1 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 2000] [Ichazo 2001] [Lu 2005] [Tserki 2005] [Nachtigall 2007] [Dominkovics 2007] [Danyadi 2010] [Ayrilmis 2011] [Acda 2012] [Islam 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 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 2008]. In particular, when applied to carbon fibres, direct fluorination led to a noticeable increase in fibre hydrophobicity [Bismarck 1997] [Dubois 2005] [Guérin 2012]. The application of direct fluorination to lignocellulosic products has been studied in the past with the intention of making Kraft paper waterproof [Sapieha 1990]. Then the surface fluorination of paper was developed using the CF_4 radio-frequency plasma technique [Sahin 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_2 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_4 or C_2F_6. 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, ^{19}F solid-state nuclear magnetic resonance (^{19}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.

2 MATERIALS AND METHODS

2.1 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 ± 0.17. The flour was sifted so that its grading was smaller than 250 µm. The polymer used to process the derived composites was unsaturated polyester Norsodyne G703, from Cray Valley, whose density was given equal to 1.17.

2.2 Direct fluorination of the wood flour

About 5g 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 2h 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_2) 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_2 gas was injected in addition to N_2 gas to reach 1 atm. The total pressure inside the closed reactor was maintained constant for 3h, and five additions of fluorine were performed in order to compensate for the consumption of molecular fluorine during the reaction. Finally, after 2h under a flow of N_2 gas at 150°C to remove all the F_2 molecules, and cooling to ambient temperature for 11h, the flour was heated again to 150°C with a flow of N_2 gas for 1h to eliminate traces of adsorbed F_2, HF, CF_4 and C_2F_6 molecules.

2.3 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 ^{19}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^{-1}), and 64 co-added scans were collected for each sample. ^{19}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 µs. 128 scans were recorded. The MAS spinning speed was set to 34 kHz, high enough to significantly average and weaken the ^{19}F-^{19}F homonuclear coupling, which is the main interaction. ^{19}F chemical shifts were externally referenced to $CFCl_3$.

2.4 TGA

The thermogravimetric analysis was performed under a nitrogen atmosphere of 0.9 bars using a PerkinElmer TGA 4000 analyser. About 10mg of wood flour was heated from 35°C 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.

2.5 SEM analysis

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

2.6 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 µm 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 x 10 mm x 1.76 mm.

2.7 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 °C for 48 h to attain the anhydrous state. Then each sample was conditioned in the humidity-controlled chambers until its weight was stabilized.

Tab. 1. Saturated salt solutions and corresponding relative humidity at 20°C.

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

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.

2.8 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 x 100 mm x 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 hours, 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.

2.9 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 (σ) and strain (ε) of the sample were calculated from the measured force (F), the sample elongation (ΔL), 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 (ε) and stress (σ) 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.

2.10 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 µL 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 24h at 80°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°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 2.9. At the time of the tests, the ambient temperature was 21°C and the relative humidity 44%.

3 RESULTS AND DISCUSSION

3.1 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 2003] [Popescu 2013]. The broad peak around 3320 cm^{-1} is due to the -OH hydroxyl groups in cellulose whereas the peak around 2900 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 cm^{-1}. The band at 1640 cm^{-1} is due to C=O stretch of aromatic ketones. The band at 1600 cm^{-1} corresponds to the C=C stretching of aromatic skeletal in lignin. C-O stretching in lignin is observed at 1260 cm^{-1}and the large peak at 1020 cm^{-1} is attributed to C-O stretching vibration.

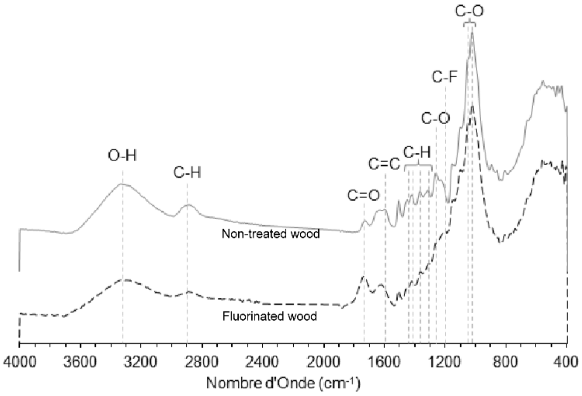

Fig. 1. FT-IR spectra of wood flours.

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 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 cm^{-1}) by carbon-fluorine (C-F) bonds (1180 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}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$_2$ or -CF$_3$ [Isbester 1997][Aimi 2004][Zhang 2010]. An example of the ^{19}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$_2$ or -CF$_3$. The broad signal at −135 ppm *vs.* CFCl$_3$ matches -CF$_2$ groups, while the signal at −182 ppm corresponds to C-F bonds and the signals at −74 and −83 ppm are both attributed to -CF$_3$ groups with different neighbours. Finally, the signal at −207 ppm is due to an aromatic -CF bond or -CHF bond. Bearing out the evidence of IR spectroscopy, NMR unambiguously highlights the presence of both fluorinated and perfluorinated groups on the wood surface.

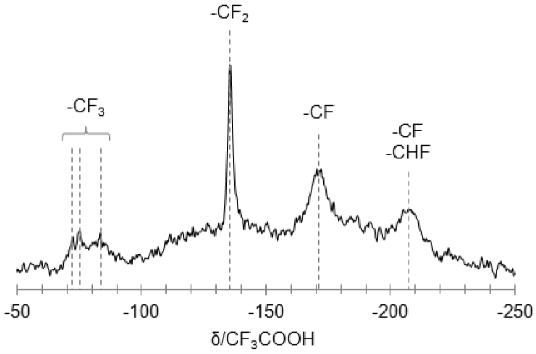

Fig. 2. ^{19}F NMR spectrum of fluorinated wood flour.

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.

3.2 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 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 5h, compared to 24h for the non-treated wood flour. 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 Tab. 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.

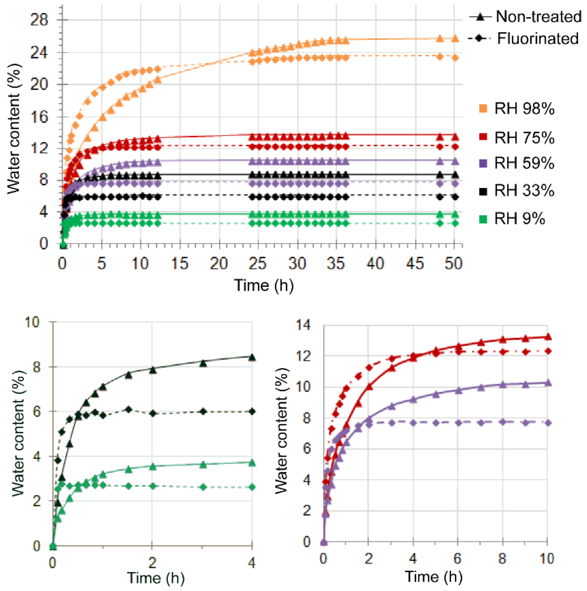

Fig. 3. Adsorption curves of the wood flour before and after fluorination for various relative humidity conditions (top: global curves; bottom: short times).

Tab. 2. Water content of the wood flours under various humidity conditions.

Relative humidity	Water content (%)		Loss of water content
	Non-treated wood	Fluorinated wood	
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 %

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 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.

3.3 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 CF_4 and C_2F_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.

3.4 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 °C due to the pressure and the N_2 atmosphere. The weight loss for the fluorinated sample between 140 °C and 220 °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 °C, in agreement with recent studies on wood thermal degradation [Jeske 2012][Poletto 2012]. The TGA data underline that the treatment is effective up to 140 °C. Since the unsaturated polyester resin is usually polymerized at 80 °C, the direct fluorination of wood flour appears to be an efficient treatment for wood flour used as a polyester composite reinforcement.

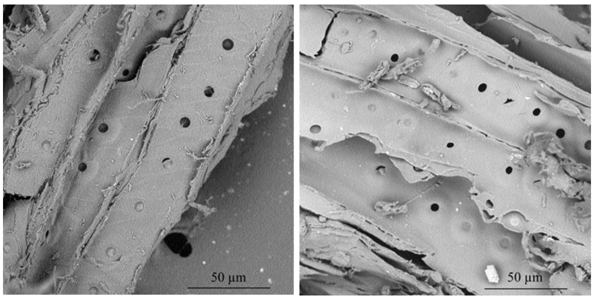

Fig. 4. SEM micrographs of an untreated (left) or a fluorinated (right) wood particle.

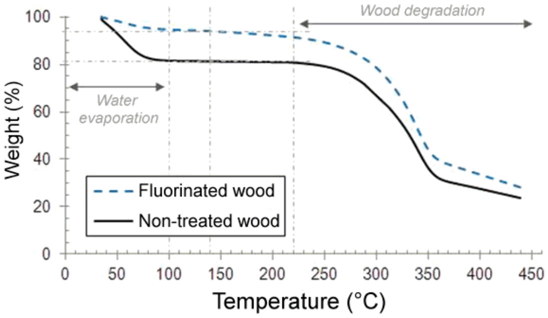

Fig. 5. TGA curves of wood flours.

3.5 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. Fig. 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.

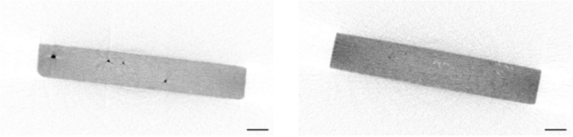

Fig. 6. X-ray tomography images of the cross-sections of two composites made of non-treated (left) or fluorinated (right) wood flours (scale bars=1 mm).

3.6 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 Tab. 3. A slight increase in the composite 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 (σ_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 to 20%).

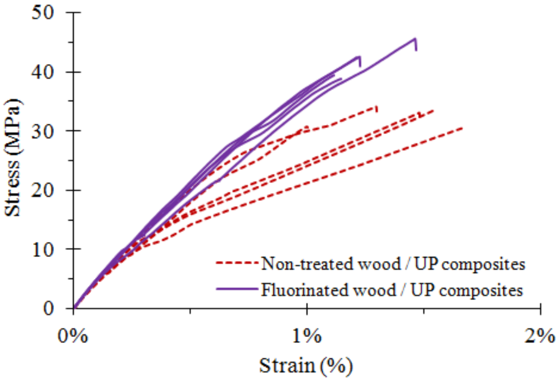

Fig. 7. Tensile stress-strain curves of composites with non-treated or fluorinated wood flours.

Tab. 3. Tensile properties of the composites with non-treated or fluorinated wood flours.

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

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 2005], whereas the addition of 1 wt.% of silane to a 30 wt.% wood reinforced polypropylene improved the composite tensile strength by 12% [Nachtigall 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 Tab. 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 increase in the flexural modulus was relatively low (+9%) [Li 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 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 3.5.

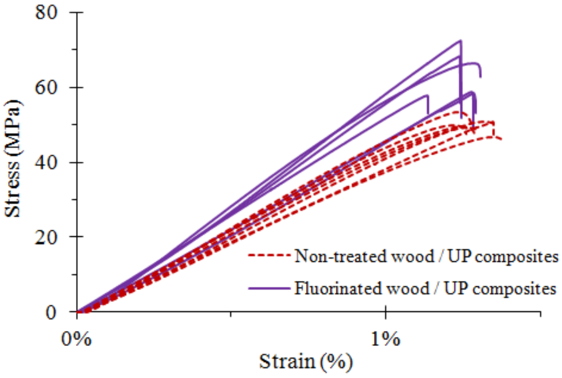

Fig. 8. Flexural stress-strain curves of composites with non-treated or fluorinated wood flours.

Tab. 4. Flexural properties of the composites with non-treated or fluorinated wood flours.

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

3.7 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 Fig. 9.

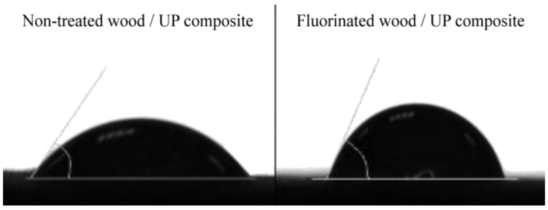

Fig. 9. Examples of contact angle images for the non-treated or fluorinated wood composites.

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° ± 13.1° to 83.6° ± 8.6°. 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.

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 2013b]. 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 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 2014]. Benzylation was proved to be very efficient to reduce the composite water uptake but at the expense of its mechanical properties [Danyadi 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 stabilization after 5h, whereas the non-treated wood flour required 24h [Saulnier 2013a].

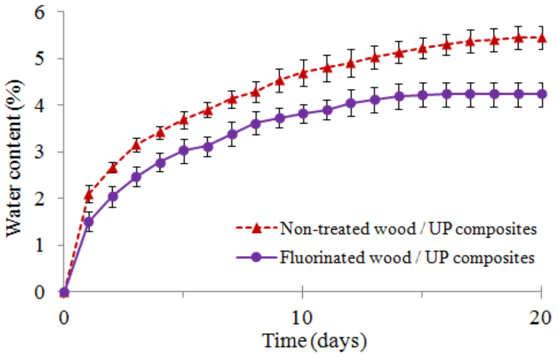

Fig. 10. Evolution of the water content of fluorinated or non-treated wood composites.

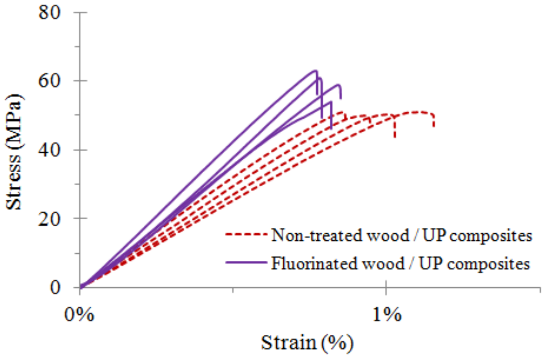

Fig. 11. Flexural stress-strain curves of composites stored 20 days under a relative humidity of 80%.

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 Tab. 5.

Tab. 5. Flexural properties of the composites stored 20 days under a relative humidity of 80%.

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

It can be noticed that the modulus 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 2010][Odegard 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.

4 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 in the wood, observed using FT-IR and ^{19}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.

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