



**HAL**  
open science

## **Fluorination renders the wood surface hydrophobic without any loss of physical and mechanical properties**

Martial Pouzet, Marc André Dubois, Karine Charlet, Alexis Béakou, Jean-Michel Leban, Mohamed Baba

### ► **To cite this version:**

Martial Pouzet, Marc André Dubois, Karine Charlet, Alexis Béakou, Jean-Michel Leban, et al.. Fluorination renders the wood surface hydrophobic without any loss of physical and mechanical properties. *Industrial Crops and Products*, 2019, 133, pp.133-141. <10.1016/j.indcrop.2019.02.044>. <hal-02181059>

**HAL Id: hal-02181059**

**<https://hal.science/hal-02181059v1>**

Submitted on 22 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC 4.0 - Attribution - Non-commercial use - International License

## **Fluorination renders the wood surface hydrophobic without any loss of physical and mechanical properties**

M. Pouzet<sup>1,2</sup>, M. Dubois<sup>1</sup>, K. Charlet<sup>2</sup>, A. Béakou<sup>2</sup>, J.M. Leban<sup>3,4</sup>, M. Baba<sup>1</sup>

<sup>1</sup> Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France

<sup>2</sup> Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut Pascal, F-63000 Clermont-Ferrand, France

<sup>3</sup> INRA, Biogéochimie des Ecosystèmes Forestiers, 54280 Champenoux

<sup>4</sup> IGN, Laboratoire de l'Inventaire Forestier, 54000 Nancy

### **Abstract**

The main limiting factor for the use of solid wood lies in its highly hydrophilic character which is associated with the loss of its properties after moisture uptake. Therefore for limiting the negative impact of moisture in wooden structures, numerous research have been carried out in order to (i) protect the surface of wood by the addition of varied varnish or protections or to (ii) modify the wooden surfaces structure by the mean of different technologies such as thermal treatments.

The former present the disadvantage to protect the wood surfaces for a limited period of time while the later present the disadvantage to reduce the mechanical properties.

Investigate how to reduce the hydrophilic character of wood without reducing physical and/mechanical properties.

We use dynamic fluorination using F<sub>2</sub> gas applied to wood samples (Douglas and silver fir) for reducing the hydrophilic character

The covalent grafting of fluorine atoms on a wood surface was highlighted by Fourier-Transform infrared spectroscopy and <sup>19</sup>F solid state Nuclear Magnetic Resonance. The wood samples acquire a hydrophobic character comparable to that of Polytetrafluoroethylene, thanks to fluorination. The high durability of this treatment was also determined by aging tests under ambient atmosphere and UV irradiation. Moreover, this treatment gives a surface with a hydrophobic character without major structural (morphology, density and colour) and mechanical modifications.

Maintaining those properties after fluorination, a dried gas/solid treatment without the use of toxic solvents and high temperatures seems to show a remarkable advantage over other physical chemical wood treatments.

**Keywords:** surface treatment, water absorption, spectroscopy, cellulose, lignin

## 1 Introduction

Wood is one of the main renewable material used for a huge number of end products such as pulp and paper, furniture, wooden frames, wooden panels etc. It is expected to be increasingly used in the emerging context of the bioeconomy, the new emerging challenge that aims at decouple the economic growth from the environmental degradations.

However, wood is a hygroscopic material especially sensitive to ambient humidity and temperature. Swelling and shrinkage caused by water absorption and desorption lead to cracks and deformation in the wood volume (1, 2, 3). Reducing wood's hydrophilic character has therefore been the subject of several studies and various treatments have been developed with this aim in mind, e.g. thermal treatment (4, 5), electric discharge (6, 7) or chemical treatment (8, 9, 10, 11, 12, 13, 14). Nevertheless, few of them are really appropriate at the industrial scale because of their toxicity, low yield or energy efficient aspects.

In this study, an original treatment at ambient temperature without toxic solvent was applied on massive wood samples.

Fluorination had already shown its efficiency on wood flour, in order to make it a good reinforcement in wood polymer composites; the gap between hydrophobicity of wood flour and the polymer matrix once reduced, the wood/polymer interface was improved (15, 16). Moreover this treatment was also applied on several natural fibres in a previous study with the aim of better understanding which wood component is most sensitive to F<sub>2</sub> gas (17). This demonstrated that the presence of lignin was necessary to achieve efficient treatment, whereas cellulose tended to inhibit the natural fibre fluorination. The present work focuses on the fluorination of massive wood samples in order to reduce its hydrophilic character. Chemical composition modifications of the wood and the impact of treatment on its structural properties were observed and discussed. The main purpose of this study is to obtain a hydrophobic from a hydrophilic wood surface, using fluorination for outdoor use. For this reason, the treatment's durability and UV irradiation were also investigated to verify the validity of this method and produce a material suitable for these applications.

## 2 Experimental

### 2.1 Fluorination

Wood samples were treated under dynamic fluorination which consists in applying a constant reactant flow through an opened passivated nickel reactor (covered with  $\text{NiF}_2$ ). Unlike the previous study on natural fibres (17), the static fluorination, based on low-pressure fluorination in a closed reactor, was not the selected process for an easier scale-up to the industrial scale. Indeed, a continuous process, without a vacuum step in a reactor, is more appropriate for continuous treatment of large pieces.

Before each fluorination, wood samples were dried under primary vacuum ( $10^{-3}$  mbar) for 1 h at  $90^\circ\text{C}$  to remove physisorbed molecules in the porosity. Simultaneously, the reactor was flushed for 1h with nitrogen gas in order to remove all traces of air and moisture. Samples were exposed to the reactive  $\text{F}_2/\text{N}_2$  (1/2 volume ratio) gaseous flow at room temperature. The fluorination durations tested were 1 min, 5 min, 10 min, 20 min, 40 min, 1 h for each wood species. After the reaction, the fluorine flow was stopped and the reactor was flushed with  $\text{N}_2$  for 1h.

### 2.2 Materials

Silver fir and Douglas fir wood samples were selected in a French sawmill located in Auvergne. The logs processed by this sawmill come from plantations harvested in the sawmill proximity. The tested samples were selected randomly and their size reduced to  $10 \times 1 \times 0.8$  cm in order to fit our experimental devices.

### 2.3 Spectroscopy analyses

FTIR spectrometer NICOLET 5700 (Thermo Electron) was used to record IR spectra using ATR mode. One hundred scans with  $4 \text{ cm}^{-1}$  resolution were collected to acquire each spectrum between  $4000$  and  $400 \text{ cm}^{-1}$ .

$^{19}\text{F}$  NMR experiments were carried out with a Bruker Avance Spectrometer with a working frequency of  $282.2 \text{ MHz}$ . A Magic Angle Spinning (MAS) probe operating with  $2.5 \text{ mm}$  rotors was used allowing a  $30 \text{ kHz}$  spinning rate. For  $^{19}\text{F}$  MAS spectra, a simple sequence was used with a single  $\pi/2$  pulse duration of  $4.0 \mu\text{s}$ .  $^{19}\text{F}$  chemical shifts were externally referenced to  $\text{CF}_3\text{COOH}$  and then referenced to  $\text{CFCl}_3$  ( $\delta_{\text{CF}_3\text{COOH}} = -78.5 \text{ ppm}$  vs  $\delta_{\text{CFCl}_3}$ ).

## 2.4 Colorimetry

The colorimetric measurement was performed with Color 45/0 Gloss Byk colorimeter. The color space of this model is based on L\* (lightness), a\* (X axis from green (-) to red (+)) and b\* (Y axis from blue (-) to yellow (+)) coordinates. The difference between two colours denoted  $\Delta E$ , representing the Euclidean distance between two colorimetric patches in the CIE L\*a\*b\* space, was calculated as follows(18, 19):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

For each sample, the colorimetric coordinates were measured four times and averaged.

## 2.5 Morphology characterization

Scanning Electron Microscopy (SEM) allowed the sample morphology investigation to evaluate the potential surface damage due to fluorination. The energy of electron beams was fixed at 15.0 kV and the working distance was over a 20 mm range.

Densitometry measurements were performed by X-ray micro densitometry equipment. The equipment was composed of an electric generator (Inel XRG3000), a X-ray tube (Siemens FK60-04 Mo, 60 kV, 2.0 kW) and a Kodak film negative Industrex type M100(20).

## 2.6 Mechanical characterization

The tensile and the flexural tests were performed on an Instron 5543 test machine equipped with a 500 N load cell at room temperature (about 24°C) and at fixed relative humidity (at 50%). The prescribed crosshead displacement rate was fixed at 1 mm/min.

Tensile tests were performed with an extensometer over 25 mm length (distance between extensometer blade) and with a manual clamping jaw. Flexural tests were performed by 3-point bending with a 50 mm gap between backings.

For each measurement, a large sample (10 x 2 x 0.8 cm) was sawed lengthwise to obtain two narrow samples (10 x 1 x 0.8 cm). One was mechanically tested without treatment as a reference and the other one after fluorination. This preparation allowed us to obtain two samples with the same morphologic profile in particular with the same growth rings. Each mechanical value was the average of six mechanical tests.

## 2.7 Hygroscopic characterization

To evaluate the hydrophilic/hydrophobic character, water contact angle measurements were performed thanks to Attension Theta Lite Optical Tensimeter with an imaging camera. A water drop was deposited on the surface of the massive wood sample. A picture was recorded when the water drop was stabilized on the surface. Contact angles were calculated as the average of five measurements taken at different locations on the sample surface.

The water sorption was investigated with an IGA sorp DVS (Dynamic Vapor Sorption) apparatus. This method, increasingly used on wood samples (21, 22, 23, 24), allowed us to follow the water intake at fixed temperatures and relative humidity. In this study, DVS measurements were operated at 30°C with a relative humidity of 30% and 60%. For this method, the sample was narrow lamella from the surface obtained by fine cutting with a scalpel. The sample thickness was between 1-2 mm for a length between 50 and 100 mm.

The water diffusion coefficient  $D$  was calculated as follow, based on Fick Second Law and Crank approximation for short experimental time (25):

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{Dt}{e^2}}$$

with  $M_t$ , the sample mass at  $t$  time

$M_\infty$ , the sample mass at hygroscopic equilibrium

$e$ , the sample thickness

## 2.8 UV light ageing

Massive wood samples were irradiated in a SEPAP 12.24 unit in the presence of air at 60°C. UV-light irradiation was carried out under polychromatic light with wavelengths higher than 300 nm (a borosilicate envelope of lamp filter wavelengths below 300 nm). Samples were placed on a rotating carousel positioned in the centre of four medium pressure 400W mercury lamps.

## 3 Results and Discussion

### 3.1 Covalent grafting of F atoms

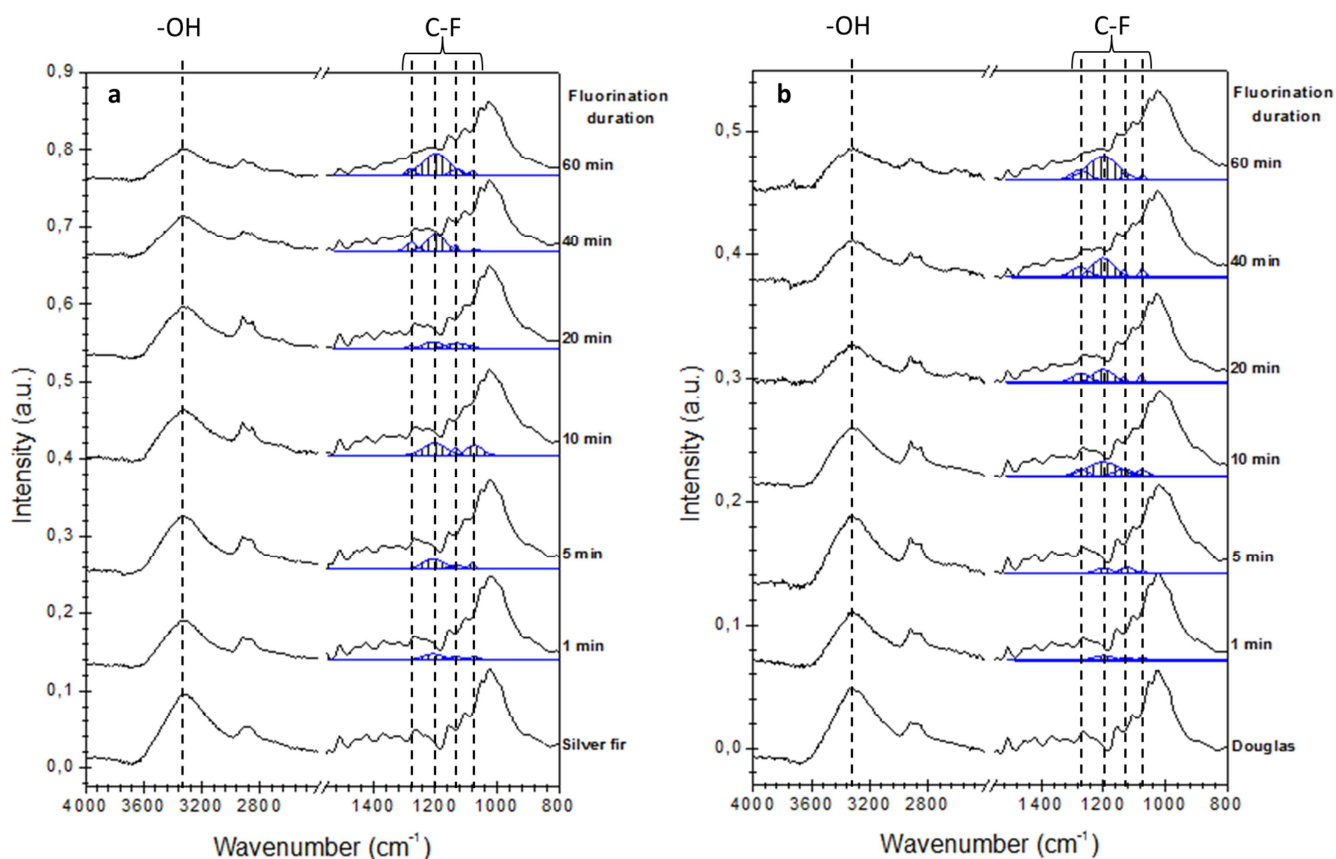
The FT-IR spectra of the wood samples before and after fluorination are shown in Figure 1. Samples are classified according to their fluorination duration. Table 1 gives the assignments of the main vibration bands (17, 26, 27, 28, 29, 30).

**Table 1.** Assignment of bands in the infrared spectra of wood samples

Assignment	Band position (cm <sup>-1</sup> )
-OH hydroxyl groups	3320
C-H stretching	2900
C=O stretching vibration of carbonyl	1730
C=O stretch in conjugated ketone	1660
O-H stretch of water absorbed	1640
C(sp <sub>2</sub> )=C(sp <sub>2</sub> ) stretch in aromatic skeleton	1600
C=C stretch in aromatic skeleton	1510
CH <sub>2</sub> deformation stretching (lignin & xylan)	1460
aromatic skeletal vibration, C-H in plane deformation	1430
C-H deformation	1370
CH <sub>2</sub> wagging	1320
Guaiacyl ring, C=O stretch	1260
-OH in plan bending	1240
C-O-C stretching	1230
C-O-C stretching	1205
C-O-C stretching	1160
C-O-C stretching	1125
C-O stretching, C-C stretching	1110
C-O deformation in primary alcohol, C=O stretching	1060
C-O ester stretching vibration	1030
C-H deformation	900

Whatever the species, wood fluorination results in the appearance of carbon-fluorine bonds, proved by the vibration bands at 1080, 1160, 1200 and 1280 cm<sup>-1</sup> (dash line on Figure 1) on FT-IR spectra. It is to be noted that the intensities and positions of CF<sub>x</sub> vibration bands (x = 1, 2 or 3) were obtained by a careful fit of the spectra and comparison with the spectrum fit of the pristine samples; an example of the fit is shown in supplementary information (Figure SI1). The fit method validity is underlined by the similar results obtained with the “difference of spectrum” method (Figure SI 2). This phenomenon is combined with a significant decrease in the hydroxyl group contribution (around 3320 cm<sup>-1</sup>). Therefore the wood fluorination consists in the substitution of -OH groups by fluorine atoms. FT-IR spectra highlight that this substitution increases in line with the fluorination duration for both wood species.

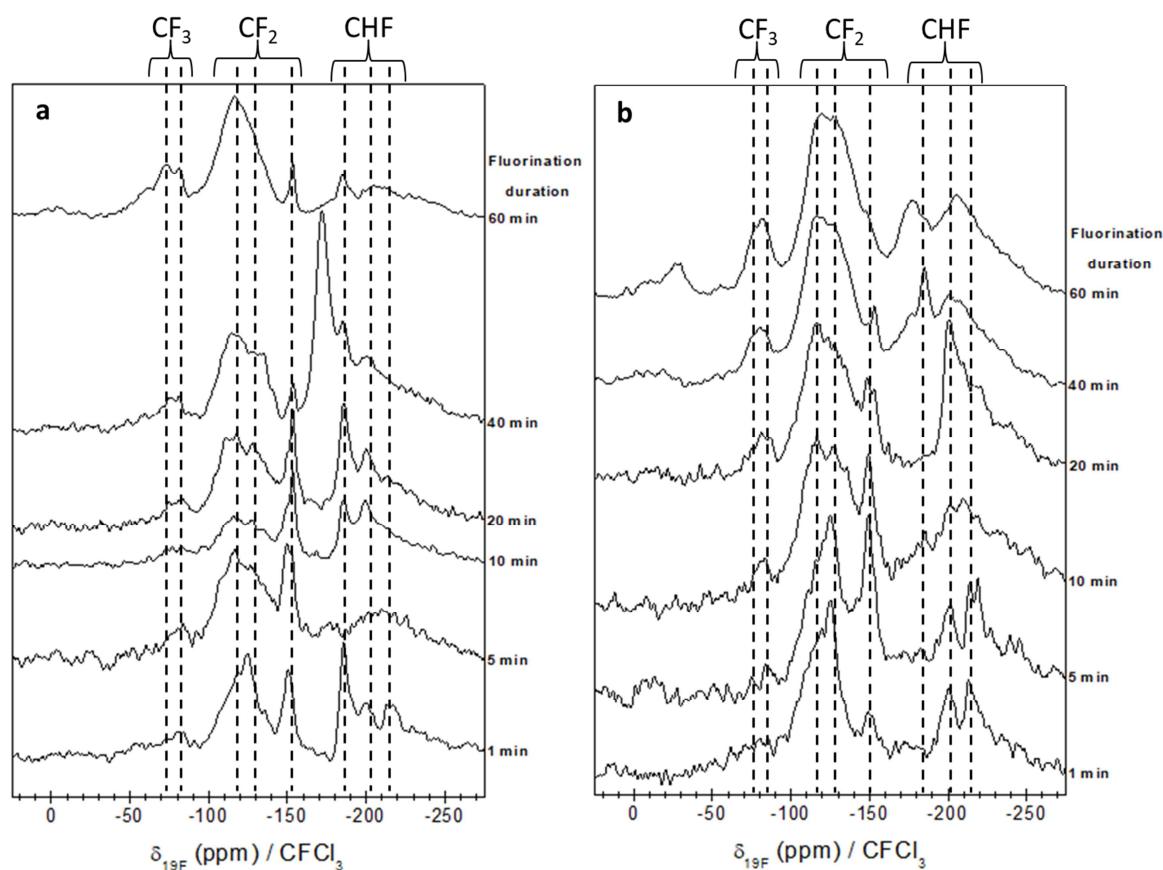
Furthermore, hydroxyl groups favour water absorption in wood because of their strong interaction with water molecules by hydrogen bonding, whereas fluorinated surfaces are known for their hydrophobic, even superhydrophobic character (15, 17, 31, 32). The substitution mentioned above suggests lower interaction between wood and water after fluorination.



**Fig.1.** FT-IR spectra of untreated and fluorinated silver fir (a) and Douglas (b) samples

$^{19}\text{F}$  NMR measurements (Figure 2) have been used to confirm the covalent grafting of fluorine atoms and to identify different fluorinated groups ( $\text{CF}_3$ ,  $\text{CF}_2$  and  $\text{CHF}$ ) present on the treated wood surface. Lines with chemical shifts at -185 and -215 ppm vs.  $\text{CFCl}_3$  evidence the presence of  $\text{CHF}$  groups, while lines at -120, -130 and -150 ppm are attributed to  $\text{CF}_2$  bonds. Different chemical shifts result from different environments, i.e. more or less fluorinated.  $\text{CF}_3$  groups are related to bands at -70 and -80 ppm (33). The identification of these fluorinated groups  $\text{CF}_3$ ,  $\text{CF}_2$  and  $\text{CHF}$  by NMR analysis confirms the covalent grafting of fluorine atoms shown by the IR spectroscopy.

NMR spectrum noise decreases with the fluorination time for the two wood species for similar recording parameters (received gain, pulse number, sample weight), thus the fluorinated groups quantity on the wood surface increases with the fluorination duration. Moreover, the relative quantity of  $\text{CF}_3$  groups increases with the treatment time. These groups were formed via the breaking of C-C chemical bonds indicating chain disruptions, i.e. material deterioration. Therefore, uncontrolled fluorination may lead to material deterioration serious enough to degrade the wood's properties (hygrometric, mechanical, morphology...).

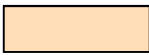









**Fig.2.**  $^{19}\text{F}$  NMR MAS (30 kHz) spectra of fluorinated silver fir (a) and Douglas (b)

Table 2 reports the colorimetric representation of CIE  $L^*a^*b^*$  of silver fir and Douglas samples before and after fluorination. These colorimetric representations underline the tendency of the treatment to brown the wood. An increase in fluorination time accentuates this browning. This colour change can be considered as a quick qualitative method to estimate the fluorination rate on wood.

Moreover  $\Delta E$  values between the colours of the samples before and after fluorination have been calculated. In the silver case, the  $\Delta E$  values are perceptible to the human eye, even after 1 min treatment, because they are higher than the reference value ( $\Delta E \geq 3$ ). However, in the Douglas case, the colour difference is notable after a longer fluorination (beyond 20 min). Furthermore, the previous study on natural fibre fluorination demonstrates the higher reactivity of silver fir towards fluorination (17). Therefore, this difference in sample colours can be explained by this reactivity difference between the two species; it may be noted that Douglas exhibits darker colour and changes are more difficult to observe than in Silver fir case. Despite  $\Delta E$  variations of the same range, colorimetric patches in Table 2 underline a more distinct colour variation in Silver fir case.

**Table 2.**Colorimetric patches of wood samples before and after fluorination

Sample	Silver fir		Douglas	
	Colour	$\Delta E$	Colour	$\Delta E$
Untreated		-		-
Fluorinated	1 min	5.83		0.67
	5 min	6.50		1.62
	10 min	9.73		2.65
	20 min	12.69		6.54
	40 min	12.89		14.52
	60 min	17.29		14.40

### 3.2 Towards permanent hydrophobic character

To estimate the interaction between samples and water molecules, the contact angle between a water drop and the wood surface has been measured. A low contact angle ( $\theta_c < 90^\circ$ ) means strong interaction and therefore a hydrophilic character, whereas a higher angle ( $\theta_c > 90^\circ$ ) reveals a hydrophobic character. Tables 3 and 4 summarize the contact angles as well as the adsorption time of a water drop onto a wood sample before and after fluorination.

**Table 3.**Contact angle and adsorption time of a water drop on the wood surface

Sample	Silver fir		Douglas	
	Contact angle	Water drop adsorption time	Contact angle	Water drop adsorption time
Untreated	65°	11 min	97°	20 min
Fluorinated	1 min	45 min	115°	45 min
	5 min	45 min	113°	50 min
	10 min	35 min	111°	50 min
	20 min	18 min	110°	25 min
	40 min	5 s	109°	15 min
	60 min	70°	10 s	83°

The hydrophilic character of the untreated silver fir is revealed by the low water contact angle (65°). Moreover, its strong affinity with the water is confirmed by the fast water drop adsorption (11 min). These two values significantly increase after a few minutes of fluorination (below 20 min) and the silver fir acquires a hydrophobic character (110-115°). The very fast water drop adsorption time of wood fluorinated longer than 20 min underlines an important deterioration of silver fir that results in the loss of water barrier properties. This deterioration, induced by an excessive fluorination rate, was evidenced by the high relative content of CF<sub>3</sub> groups underlining severe chain disruptions.

The Douglas fluorination results in a similar contact angle and adsorption time of the water drop. However, contrary to silver fir, the Douglas sample exhibits an intrinsic hydrophobic character. Therefore, the difference between hygroscopic properties before and after fluorination is limited. Despite this difference, the impact of fluorination time on water/surface interaction is similar for the two species: the wood acquires hydrophobicity after a fluorination treatment thanks to the conversion of C-OH groups into C-F bonds.

Following this analysis, the optimal fluorination time has been estimated according to the following criteria:

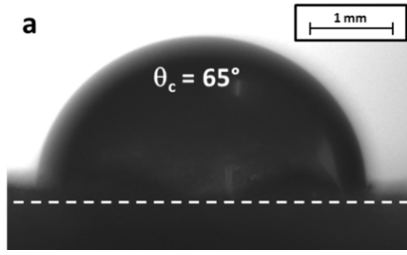
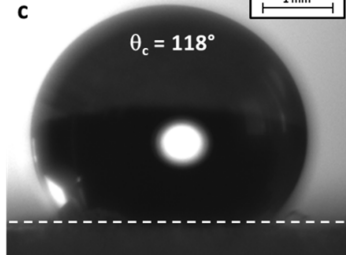
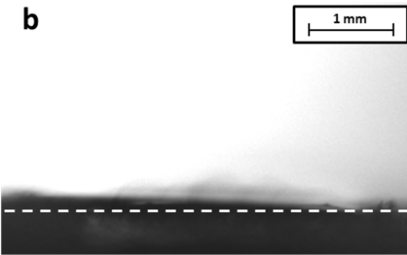
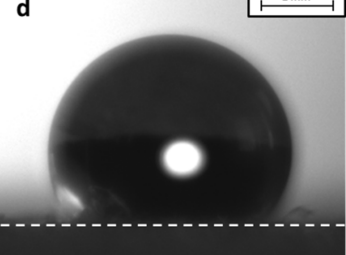
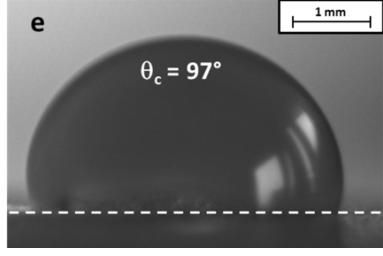
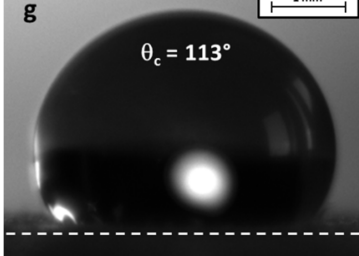
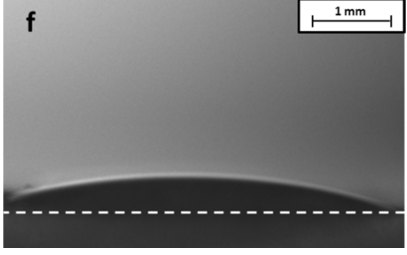
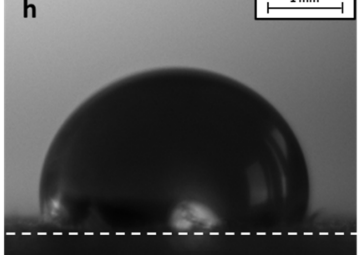
- The hydrophobic character obtained after fluorination. The optimal time is thus below 20 minutes based on the Table 3 values.

- The most favourable for the industrial scale. The treatment duration has to be as short as possible.

- The chemical composition homogeneity on the wood surface that was investigated by IR spectroscopy (cf. Figures SI 3 and SI 4 in Supporting Information). Indeed, a 1 min fluorination appears too short to allow fluorine diffusion overall the wood surface. According to the experimental parameters used, a chemical composition gradient was recorded: the region located near the gas inlet exhibits higher fluorinated groups than the opposite side.

For these reasons, the optimal wood fluorination time has been estimated at five minutes for the two species. Table 4 shows photographs of a water drop on the wood surface before and after optimal fluorination at different times after the drop is deposited. The treatment's impact on the water affinity of wood is obvious.

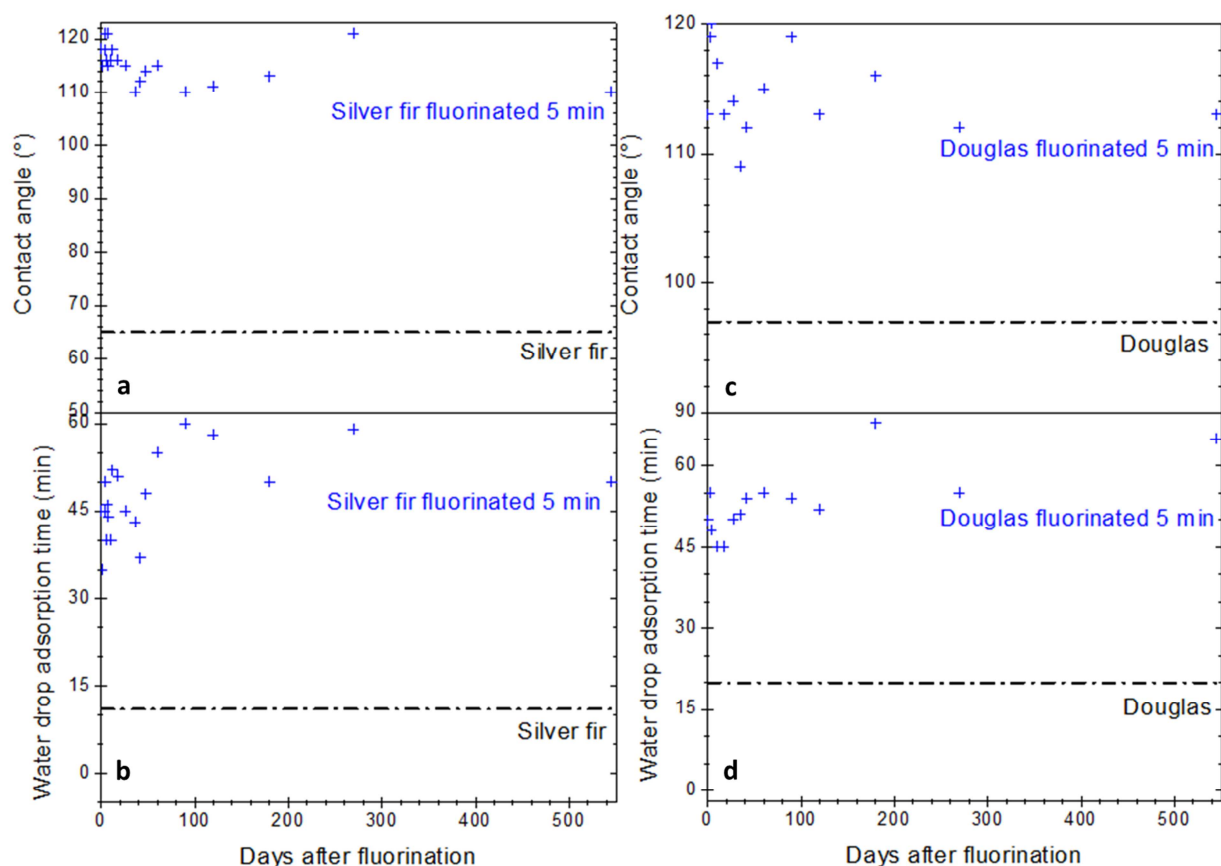
**Table 4.** Contact angle of water drop on pristine and fluorinated (5 min at room temperature) wood

Sample	Untreated	Fluorinated 5 min
Silver fir	2s after the water drop deposit 	2s after the water drop deposit 
	15 min after the water drop deposit 	15 min after the water drop deposit 
Douglas	2s after the water drop deposit 	2s after the water drop deposit 
	20 min after the water drop deposit 	20 min after the water drop deposit 

To estimate the treatment's durability, the time dependence of the hydrophobic behaviour of wood samples has been investigated regularly according to their fluorination. Figure 3 displays the evolution of the contact angle between a water drop and the wood surface (silver fir and Douglas) fluorinated for 5 minutes. For both wood species, the contact angle between water and treated wood is still unchanged between 110 and 120° even 2 years after treatment. Moreover, Figure. 3 shows the evolution of a water drop adsorption time on a fluorinated wood surface. This adsorption time is always higher on treated wood (between 35 and 60 min

in the silver fir case and between 45 and 90 min for the Douglas sample) than on the virgin sample (around 15 min for the two species). These measurements were carried out under ambient atmosphere, thus relative humidity and temperature variations may explain the difference between the adsorption times. Indeed, water evaporation competes for this recording time and is related to relative humidity and temperature.

The hydrophobic character of fluorinated wood under an ambient atmosphere is stable even 2 years after the treatment which suggests a relative degree of sustainability.



**Fig.3.** Changes in the contact angle of a water drop on Silver fir (a) and Douglas (c); water drop adsorption time onto silver fir (b) and Douglas (d) at ambient atmosphere in relation to ageing time

The change in the water contact angle for samples irradiated under UV has also been measured. Figure 4 displays the difference between the contact angles before and after wood fluorination (denoted  $\Delta_{\text{angle}}$ ) at different irradiation times. Colour lines were added as an eye guide. The horizontal dash line is the orthogonal projection for  $\Delta_{\text{angle}}$  equal to zero, i.e. no difference in comparison with the pristine wood and no gain in hydrophobicity. Firstly, the tendency curves plotted on Figure 4 are more or less parallel. This parallelism underlines the fact that hydrophobicity change under UV irradiation is the same for fluorinated and untreated

wood. In other words, the wood's photodegradation is not impacted (accelerated or slowed) by the fluorination. Secondly, tendency curves evidence that fluorination is more efficient for silver fir than for Douglas. This difference may be explained by the higher reactivity to  $F_2$  of silver fir than of Douglas. The higher this reactivity, the higher the contact angle. The return to the original hydrophilic character ( $\Delta_{\text{angle}} = 0$ ) is thus longer for silver fir than for Douglas due to a higher  $\Delta_{\text{angle}}$  before UV irradiation (at exposure time = 0 hr).

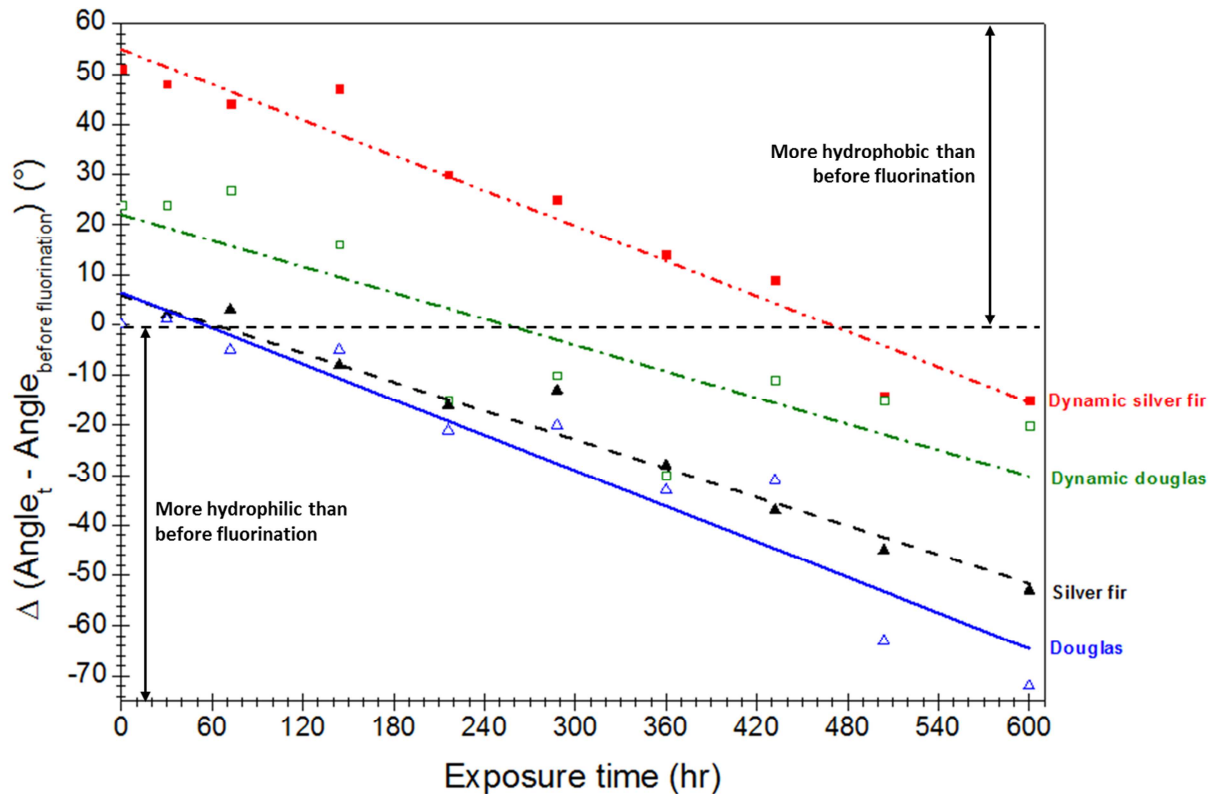










Fig.4. Evolution of contact angle between a water drop and wood samples under UV irradiation

The fluorination impact on the colour change under UV irradiation has also been estimated. Table 5 summarizes the colour of virgin and fluorinated woods before and after UV irradiation (for 600hrs). Such long UV irradiation implies an important browning of wood samples as revealed by the high  $\Delta E$  value 25.31 and 17.6. For the Douglas case,  $\Delta E$  is lower than in the silver fir case. This difference can be explained by the silver fir's lighter colour. Furthermore,  $\Delta E$  values between irradiated and non-irradiated wood are similar (silver fir) or close (Douglas) underlining the fact that fluorination does not act on the wood colour change under UV irradiation.

**Table 5.** Colorimetric patches of virgin and fluorinated wood samples after UV irradiation

Sample	UV irradiation	Silver fir		Douglas	
		Colour	$\Delta E$	Colour	$\Delta E$
Untreated	0 hr		25.31		17.69
	600 hrs				
Dynamic fluorination	0 hr		25.72		13.55
	600 hrs				

To support the fact that wood fluorination leads to a hydrophobic wood surface, water sorption measurements have been performed. Figure 5 shows the DVS profiles of wood samples at fixed relative humidity (RH = 30 and 60%) at 30°C. These analyses reveal that water adsorption of fluorinated wood is lower after the fluorination for the two RH. The moisture content at the hygroscopic equilibrium is decreased thanks to the fluorination whatever the wood species used. A 20% decrease is observed for silver fir and Douglas, respectively at RH of 60%. The higher the RH, the higher the percentage decreases after fluorination.

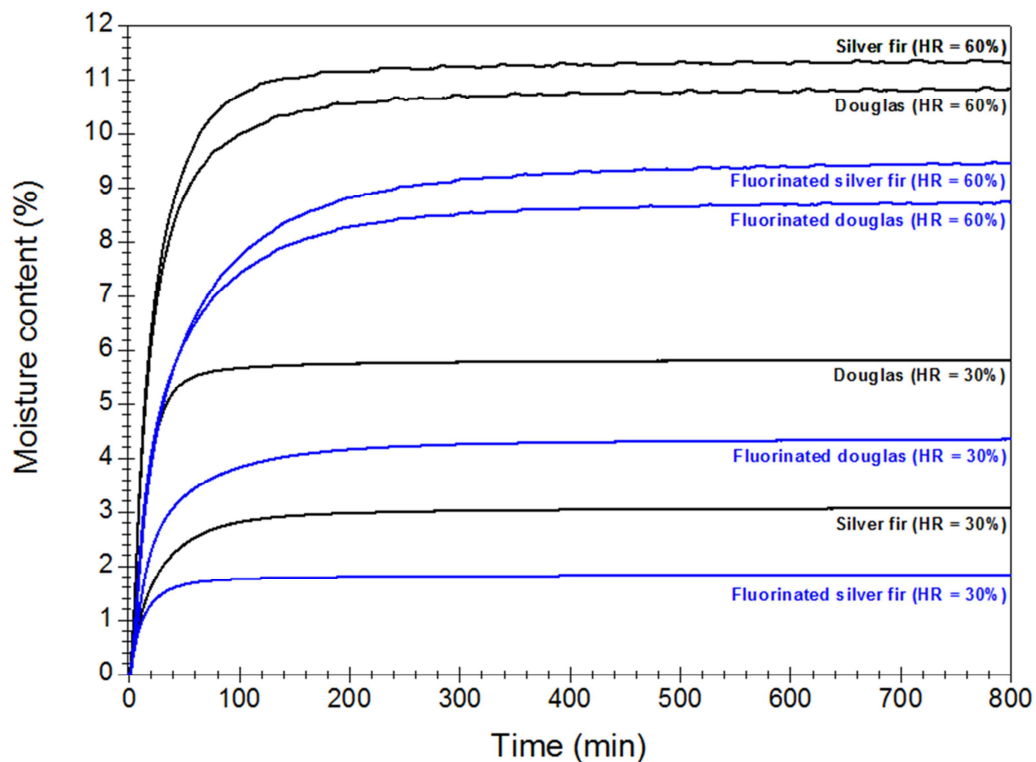
**Fig.5.** Dynamic Vapour Sorption of untreated (black lines) and fluorinated (blue lines) wood at fixed relative humidity (30% and 60%) and temperature (30°C)

Table 6 displays the water diffusion coefficient values of the two wood species at fixed relative humidity (RH = 30 and 60 %). These values reveal a faster water absorption in fluorinated wood case than in virgin material one. Therefore, the fluorinated wood reaches faster its hygroscopic and its equilibrium moisture content (EMC).

Indeed, on one side the EMC reduction after fluorination is certainly due to the diminution of available absorption sites of massive wood. On the other hand, the kinetic increase of water absorption can be explained by the presence of microscopic diffusion pipes which may create during the fluorination. Water may migrate easily into these pipes thanks to the fluorine atoms presence.

**Table 6.** Water diffusion coefficient of virgin and fluorinated wood ( $\text{m}^2.\text{s}^{-1}$ )

Sample	Silverfir		Douglas	
	Raw	Fluorinated (5 min, RT)	Raw	Fluorinated (5 min RT)
RH				
30%	$1,87.10^{-10}$	$5,32.10^{-10}$	$3,66.10^{-10}$	$4,43.10^{-10}$
60%	$2,19.10^{-9}$	$2,22.10^{-9}$	$1,15.10^{-9}$	$2,06.10^{-9}$

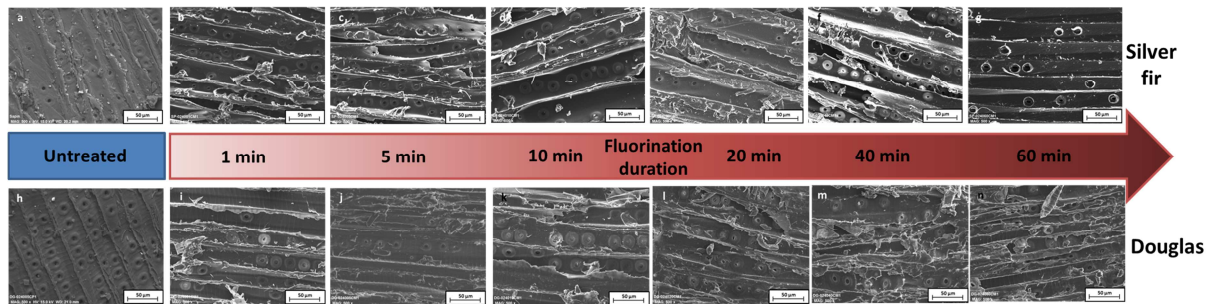
The fluorination of wood allows a durable hydrophobic character under ambient atmosphere to be obtained. This treatment does not accelerate or slow the wood's photodegradation (taking into account hydrophobicity and colorimetric data) and appears efficient at several relative humidities in decreasing the water adsorption. Nevertheless, to be fully effective, fluorination must not generate too much mechanical and structural damage. Therefore, these properties have also been investigated after fluorination.

### 3.3 Withwood structural conservation

#### 3.3.1 Morphology and density

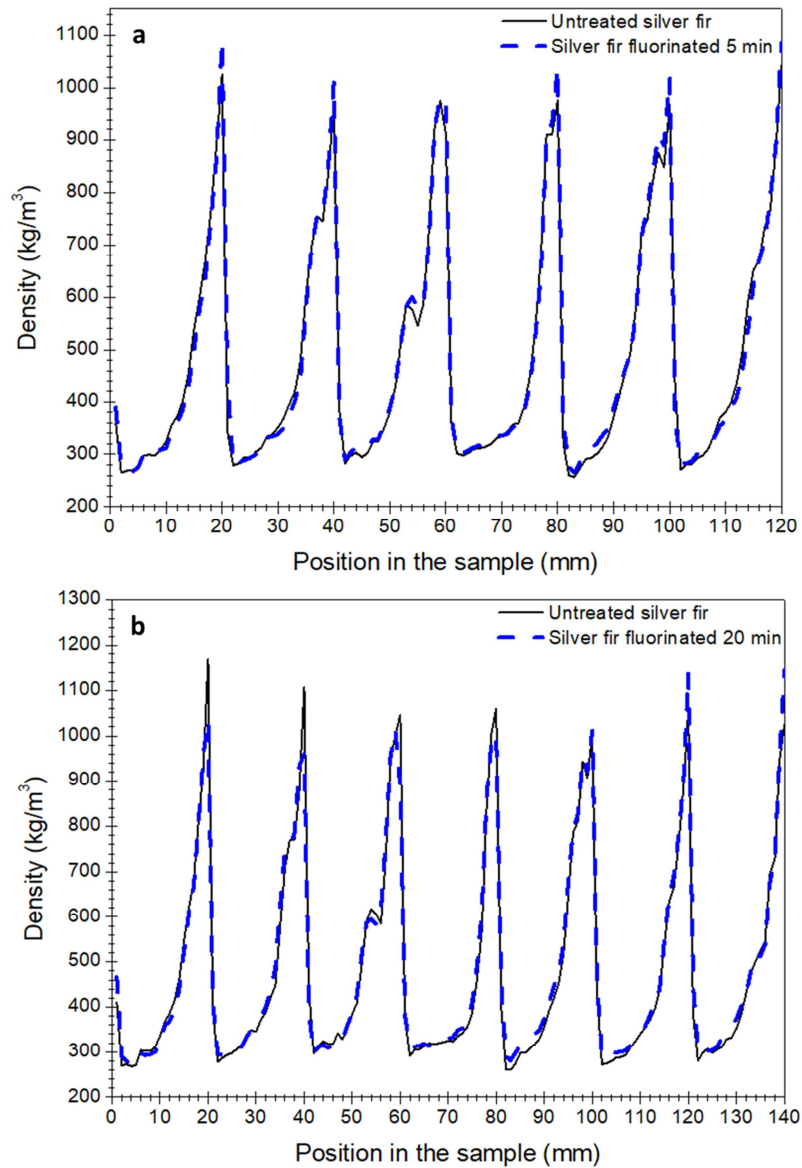
The superficial structure of wood has been checked by SEM (Figure 6). The fluorine atoms grafted onto the wood surface do not lead to major changes for short fluorination durations. However, a 20 min treatment implies the initiation of surface deterioration that is revealed by some strongly deteriorated tracheid. This fluorination duration corresponds to a deterioration in the wood's water barrier properties. This surface damage and the resulting decrease in the hydrophobic character may be explained by chain disruptions (C-C bonds rupture) highlighted by  $\text{CF}_3$  group presence on the NMR spectra. Longer fluorinations induce increasing damage

on wood structures and consequently, both low contact angles and faster water drop adsorption.



**Fig. 6.** Scanning electron micrographs of pristine and fluorinated wood

To evaluate the fluorination impact on the wood volume, densitometry measurements have been performed on silver fir before and after treatment. Figure 7 presents the intraring wood density profiles of samples fluorinated for 5 and 20 min. A density peak corresponds to late wood rings (denser rings) and the lower density reveals early wood rings (less dense) presence. The density profiles of pristine and fluorinated wood overlap whatever the treatment duration. Such data unambiguously show that reaction with  $F_2$  gas in the prescribed conditions is a surface treatment in accordance with SEM images.



**Fig.7.** Density profile of virgin silver fir (black line) and silver fir fluorinated for 5 min (a –dash blue line) and 20 min (b –dash blue line)

### 3.3.2 Mechanical properties

Maintaining the mechanical properties is one of the objectives of the present work contrary to thermal treatments which are known for their mechanically detrimental effect (5). Tensile and flexural properties are given in Table 7. The tensile modulus of elasticity and the strength are similar before and after the wood treatment taking into account standard deviation measurement. The notable difference between the tensile modulus of elasticity for untreated and fluorinated silver fir is mainly due to the samples' wide disparity. The high accuracy

(more than 200 MPa) underlines this disparity. As for the tensile tests, the flexural property values before and after fluorination are similar for all wood species.

The similitude between pristine and treated samples demonstrates that the fluorination does not necessarily lead to a loss of mechanical properties in the wood. More specifically, the modulus of elasticity conservation proves that wood samples have not been subject to volumetric mechanical damage, while similar strength confirms that the mechanical surface properties, (e.g. no crack appears on the surface) have been maintained.

**Table 7.** Tensile and flexural properties of untreated and fluorinated wood

Sample		Silver fir		Douglas	
		Untreated	Fluorinated 5 min at RT	Untreated	Fluorinated 5 min at RT
Tensile	Modulus of elasticity (MPa)	699±276	599±214	348 ± 66	381 ± 129
	Strength (MPa)	3.5 ± 0.9	3.6 ± 0.5	3.4 ± 0.4	3.5 ± 0.6
Flexural	Modulus of elasticity (MPa)	332 ± 106	342 ± 94	338 ± 46	328 ± 38
	Strength (MPa)	6.2 ± 1.0	6.6 ± 1.0	8.8 ± 1.3	8.4 ± 1.1

#### 4 Conclusion

Fluorination, a surface treatment based on a heterogeneous gas/solid reaction was applied to massive wood to sustainably increase its hydrophobicity. Firstly, the wood fluorination results in the substitution of –OH groups by covalent fluorine atoms as proved by FTIR and <sup>19</sup>F NMR spectroscopies. Such chemical composition changes were accompanied by wood browning; the higher the fluorination duration, the higher the chemical conversion on the surface and the samples appear to brown significantly.

The treated wood exhibited a lower affinity for water. Indeed, the water contact angles were higher after a short fluorination time (lower than 20 min). The water drop adsorption into treated wood was also slowed down in comparison with the pristine sample. The DVS analysis confirmed the hydrophobic character and lower absorption efficiency towards water vapour. Moreover, the fluorinated layer durability was evaluated under ambient atmosphere and UV irradiation. The fluorinated woods exhibit a hydrophobic character even two years after its treatment when stored under ambient atmosphere. In addition, the treatment did not

have a measurable impact on the wood's photodegradation. The latter point was supported by the similar  $\Delta E$  values between fluorinated and pristine woods after long term UV irradiation. SEM underlined the integrity of the wood's superficial structure for short term treatment (lower than 20 minutes). For longer treatments, increasingly, wood cell degradation was observed. The surface location of the fluorinated layer is evidenced by the wood density profiles that were not impacted by optimal treatment (5 min fluorination) and the mechanical properties were also preserved. Therefore, a short fluorination (around 5 min) led to a durable hydrophobic character by fluorine covalent grafting to be reached for two wood species, silver fir and Douglas, with no significant structural modifications.

## Acknowledgments

The authors wish to thank the photochemistry team of the Institut de Chimie de Clermont Ferrand (ICCF) for their help during the experimental phase. We express our gratitude to the Conseil Régional d'Auvergne for funding this project.

## References

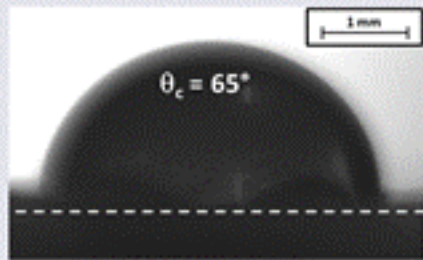
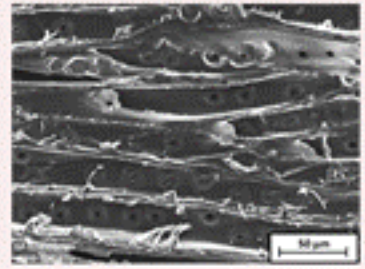
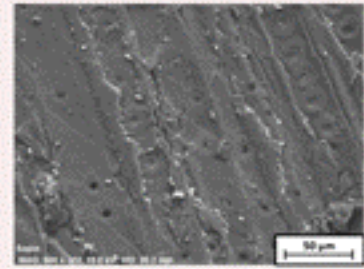
- (1) Kollman, F. F. P.; Côté, W. A., *Principles of Wood Science and Technology : Solide Wood*. Springer Berlin Heidelberg ed.; 1968; p 592.
- (2) Derome, D.; Rafsanjani, A.; Patera, A.; Guyer, R.; Carmeliet, J., Hygromorphic Behaviour of Cellular Material: Hysteretic Swelling and Shrinkage of Wood Probed by Phase Contrast X-Ray Tomography. *Philosophical Magazine* **2012**,*92* (28-30), 3680-3698.
- (3) Patera, A.; Derome, D.; Griffa, M.; Carmeliet, J., Hysteresis in Swelling and in Sorption of Wood Tissue. *Journal of Structural Biology* **2013**,*182* (3), 226-234.
- (4) Stamm, A. J.; Burr, H. K.; Kline, A. A., Staybwood—Heat-Stabilized Wood. *Industrial & Engineering Chemistry* **1946**,*38* (6), 630-634.
- (5) Mburu, F.; Dumarçay, S.; Bocquet, J. F.; Petrissans, M.; Gérardin, P., Effect of Chemical Modifications Caused by Heat Treatment on Mechanical Properties of Grevillea Robusta Wood. *Polym. Degrad. Stabil.* **2008**,*93* (2), 401-405.
- (6) Podgorski, L.; Chevet, B.; Onic, L.; Merlin, A., Modification of Wood Wettability by Plasma and Corona Treatments. *Int. J. Adhes. Adhes.* **2000**,*20* (2), 103-111.
- (7) Lux, C.; Szalay, Z.; Beikircher, W.; Kováčik, D.; Pulker, H. K., Investigation of the Plasma Effects on Wood after Activation by Diffuse Coplanar Surface Barrier Discharge. *European Journal of Wood and Wood Products* **2013**,*71* (5), 539-549.
- (8) Ashori, A.; Babaei, M.; Jonoobi, M.; Hamzeh, Y., Solvent-Free Acetylation of Cellulose Nanofibers for Improving Compatibility and Dispersion. *Carbohydr. Polym.* **2014**,*102*, 369-375.
- (9) Chowdhury, M. J. A.; Humphrey, P. E., The Effect of Acetylation on the Shear Strength Development Kinetics of Phenolic Resin-to-Wood Bonds. *Wood Fiber Sci.* **1999**,*31* (7), 293-299.

- (10) Jonoobi, M.; Harun, J.; Mathew, A. P.; Hussein, M. Z. B.; Oksman, K., Preparation of Cellulose Nanofibers with Hydrophobic Surface Characteristics. *Cellulose* **2010**,*17* (2), 299-307.
- (11) Tserki, V.; Zafeiropoulos, N. E.; Simon, F.; Panayiotou, C., A Study of the Effect of Acetylation and Propionylation Surface Treatments on Natural Fibres. *Compos. Pt. A-Appl. Sci. Manuf.* **2005**,*36* (8), 1110-1118.
- (12) Youngquist, J. A.; Krzysik, A.; Rowell, R., Dimensional Stability of Acetylated Aspen Flakeboard. *Wood Fiber Sci.* **1986**,*18* (1), 90-98.
- (13) Kazayawoko, M.; Balatinecz, J. J.; Woodhams, R. T.; Sodhi, R. N. S., X-Ray Photoelectron Spectroscopy of Lignocellulosic Materials Treated with Maleic Anhydride Polypropylenes. *Journal of Wood Chemistry and Technology* **1998**,*18* (1), 1-26.
- (14) Mohebbi, B.; Fallah-Moghadam, P.; Ghotbifar, A. R.; Kazemi-Najafi, S., Influence of Maleic-Anhydride-Polypropylene (Mapp) on Wettability of Polypropylene/Wood Flour/Glass Fiber Hybrid Composites. *Journal of Agricultural Science and Technology* **2011**,*13* (Number 6), 877-884.
- (15) Pouzet, M.; Gautier, D.; Charlet, K.; Dubois, M.; Béakou, A., How to Decrease the Hydrophilicity of Wood Flour to Process Efficient Composite Materials. *Appl. Surf. Sci.* **2015**,*353*, 1234-1241.
- (16) Saulnier, F.; Dubois, M.; Charlet, K.; Frezet, L.; Beakou, A., Direct Fluorination Applied to Wood Flour Used as a Reinforcement for Polymers. *Carbohydr. Polym.* **2013**,*94* (1), 642-646.
- (17) Pouzet, M.; Dubois, M.; Charlet, K.; Béakou, A., The Effect of Lignin on the Reactivity of Natural Fibres Towards Molecular Fluorine. *Materials & Design* **2017**,*120*, 66-74.
- (18) Sgarbossa, A.; Costa, C.; Menesatti, P.; Antonucci, F.; Pallottino, F.; Zanetti, M.; Grigolato, S.; Cavalli, R., Colorimetric Patterns of Wood Pellets and Their Relations with Quality and Energy Parameters. *Fuel* **2014**,*137*, 70-76.
- (19) Tolvaj L., F. O., Artificial Ageing of Wood Monitored by Drift Spectroscopy and Cie L\*a\*B\* Color Measurements. *Holzforschung - International Journal of the Biology, Chemistry, Physics and Technology of Wood* **1995**,*49* (5), 397-404.
- (20) Leban, J. M.; Pizzi, A.; Wieland, S.; Zanetti, M.; Properzi; Pichelin, F., X-Ray Microdensitometry Analysis of Vibration-Welded Wood. *Journal of Adhesion Science and Technology* **2004**,*18* (6), 673-685.
- (21) Hill, C. A. S.; Norton, A. J.; Newman, G., The Water Vapour Sorption Properties of Sitka Spruce Determined Using a Dynamic Vapour Sorption Apparatus. *Wood Sci. Technol.* **2010**,*44* (3), 497-514.
- (22) Hill, C. A. S.; Ramsay, J.; Keating, B.; Laine, K.; Rautkari, L.; Hughes, M.; Constant, B., The Water Vapour Sorption Properties of Thermally Modified and Densified Wood. *J. Mater. Sci.* **2012**,*47* (7), 3191-3197.
- (23) Popescu, C.-M.; Hill, C. A. S., The Water Vapour Adsorption–Desorption Behaviour of Naturally Aged Tilia Cordata Mill. Wood. *Polym. Degrad. Stabil.* **2013**,*98* (9), 1804-1813.
- (24) Sharratt, V.; Hill, C. A. S.; Zaihan, J.; Kint, D. P. R., Photodegradation and Weathering Effects on Timber Surface Moisture Profiles as Studied Using Dynamic Vapour Sorption. *Polym. Degrad. Stabil.* **2010**,*95* (12), 2659-2662.
- (25) Crank, J., *The Mathematics of Diffusion*. Oxford University Press: London, 1975.
- (26) Bodirlau, R.; Teaca, C. A., Fourier Transform Infrared Spectroscopy and Thermal Analysis of Lignocellulose Fillers Treated with Organic Anhydrides. *Rom. J. Phys.* **2009**,*54* (1-2), 93-104.
- (27) Chen, H.; Ferrari, C.; Angiuli, M.; Yao, J.; Raspi, C.; Bramanti, E., Qualitative and Quantitative Analysis of Wood Samples by Fourier Transform Infrared Spectroscopy and Multivariate Analysis. *Carbohydr. Polym.* **2010**,*82* (3), 772-778.
- (28) 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.
- (29) Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B., Effects of Short-Time Vibratory Ball Milling on the Shape of Ft-Ir Spectra of Wood and Cellulose. *Vib. Spectrosc.* **2004**,*36* (1), 23-40.

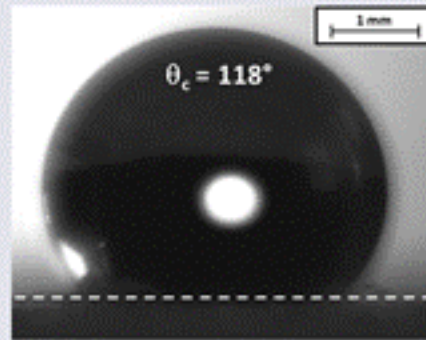
- (30) Traoré, M.; Kaal, J.; Martínez Cortizas, A., Application of Ftir Spectroscopy to the Characterization of Archeological Wood. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2016**,*153*, 63-70.
- (31) Di Mundo, R.; Palumbo, F.; d'Agostino, R., Influence of Chemistry on Wetting Dynamics of Nanotextured Hydrophobic Surfaces. *Langmuir* **2010**,*26* (7), 5196-5201.
- (32) Wu, J.; Xia, J.; Lei, W.; Wang, B.-p., Fabrication of Superhydrophobic Surfaces with Double-Scale Roughness. *Materials Letters* **2010**,*64* (11), 1251-1253.
- (33) Dubois, M.; Giraudet, J.; Guerin, K.; Hamwi, A.; Fawal, Z.; Pirotte, P.; Masin, F., Epr and Solid-State Nmr Studies of Poly(Dicarbon Monofluoride) (C<sub>2</sub>f)(N). *J. Phys. Chem. B* **2006**,*110* (24), 11800-11808.



Conservation of structure and colour of wood

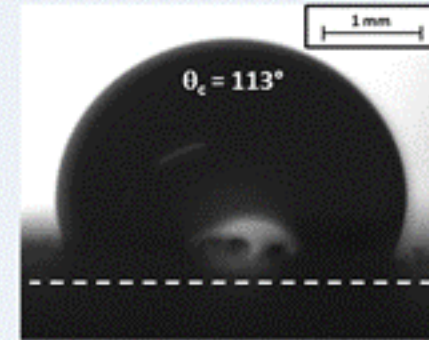


Fluorination - 5 min

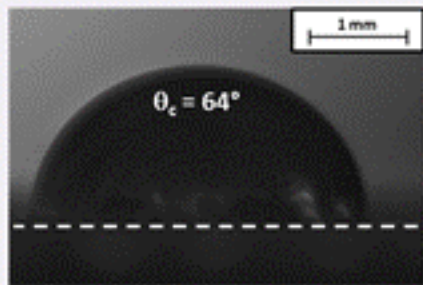


Durable hydrophobic character

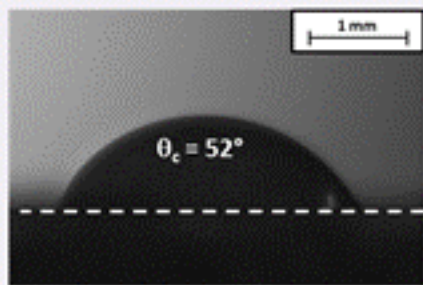
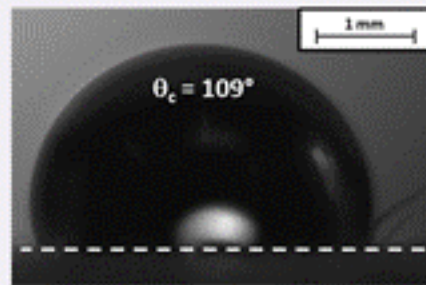
2 years after the treatment



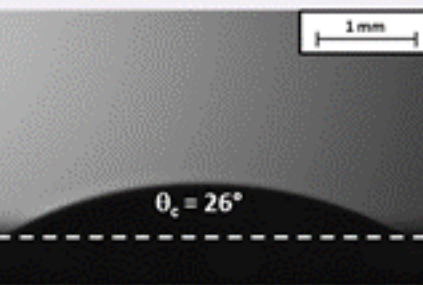
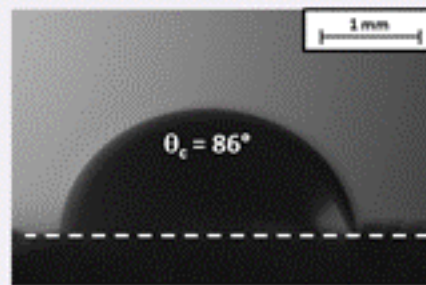
UV Irradiation



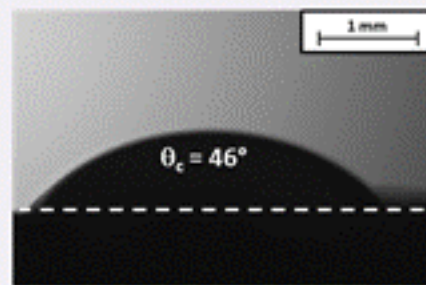
72hr



288hr



600hr



Similar photodegradation kinetic