Can supercritical carbon dioxide be suitable for the green pretreatment of plant fibres dedicated to composite applications?

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Abstract:

This work explores the use of supercritical carbon dioxide (sc-CO_2) conditions as an innovative and environmentally friendly treatment of plant fibres to optimize their performance for integration into composite materials. This study evaluates, in particular, the influence of this treatment on the mechanical, thermal, hygroscopic properties and biochemical features of industrial hemp bast fibres. Two distinct settings were tested by tuning time, temperature and pressure parameters to assess the influence of the severity of the treatment on the fibre quality. Results show that sc-CO_2 treatment induces an

increase in the fibre fineness and a decrease in their moisture sensitivity while maintaining their initial resistance to temperature. These changes are consistent with the measured decrease in the relative content of hemicelluloses. A significant decrease in the tensile rigidity and strength is also observed as a function of the severity of sc-CO$_2$ treatment, counterbalancing a little bit the benefits retained on the other properties.

Keywords: Hemp fibres, Supercritical carbon dioxide, Biocomposite application, Hygroscopic power, Mechanical properties

1. Introduction

The development of plant fibres composites (PFCs) arouses currently a significant focus in industry and academia. Indeed, inherent properties such as low density, biodegradability and high specific mechanical properties make plant fibres an attractive option for composite application [1, 2]. In this way, PFCs are gaining interest and their market shares are growing in various industrial sectors, such as transport, design, acoustics, sport and leisure. Nevertheless, some of their intrinsic features, such as moisture sensitivity, and their intricate processing (including extraction from plant and transformation stages), still remain major impediments to the development of high-grade and durable composites. Anyways, several parameters can be tuned and controlled at the scale of the plant fibres themselves using efficient treatment processes, in order to improve the performance of PFCs. Indeed, even if the PFCs properties, as for all multiphasic materials, are dependent on the properties of the matrix itself, the most influential parameters are mainly related to the fibre properties, in particular their mechanical and surface properties, thermal resistance, their orientation, length, content, fineness, dispersion and affinity for the polymeric matrix which determines the adherence [3]. Plant fibre fineness is a key parameter and several studies concluded that well separated fibres are recommended for high-performance composites [4, 5]. Indeed, bundles of fibres have lower mechanical properties than single fibres [6] and the presence of the middle lamella (in bundles) can induce an early damage in composite [7]. The hydrophilic character and the hygroscopy of the plant fibres represent also one of the main barrier for their use in composites. Indeed, the moisture sensitivity of the fibres can limit the resistance at the interface with the matrix [8, 9]. Fibre water uptake

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or desorption in composite when exposed to moisture variations may cause significant swelling and shrinkage and thus irreversible damages within the composite material, reducing both the dimensional stability and the durability of PFCs. It can also induce a degradation of the fibres themselves by biological agents including mainly bacteria and fungi. The hydrophilic character can also alter the wetting properties, and thus depending on the matrix, and in particular on its polarity, impede the impregnation of plant fibre reinforcements during the composite fabrication [10]. Hydroxyl groups present in pectic substances and hemicellulose are the main components that contribute to the fibres' moisture sensitivity. Therefore, their removal can alleviate the fibre hygroscopy and thus enhance their properties for successful use in PFCs.

So, fibre individualisation and the reduction of their moisture sensitivity while retaining good thermal and mechanical performance are the main challenge when preparing plant fibres for composite applications.

Therefore, numerous studies were and are still conducted to facilitate fibre extraction and individualization, modify, enhance, and tune their properties to meet as best as possible the composite application requirements. This is generally achieved using physical, chemical and/or enzymatic treatments. Liu et al. [3] proposed recently an excellent review of the pre-treatments envisioned and developed up to now for hemp bast fibres. It critically and comprehensively assesses the treatment processes and data available for producing well separated hemp bast fibres having optimal chemical and physical properties for best mechanical and durability properties of PFCs. It also turns out that one of the major remaining challenges is to develop a pre-treatment process that succeeds in enhancing the fibre properties while retaining an optimal cost and minimising its environmental footprint.

In such a context, the use of supercritical fluids could be an efficient process. Supercritical carbon dioxide (sc-CO_2) is a fluid state of carbon dioxide where it is held at or above its critical point (31°C – 73.8 bar). In its supercritical state, carbon dioxide (CO_2) constitutes a "green" solvent with specific properties, recyclable and non-toxic, while remaining inexpensive [11]. Combining a vapour-like viscosity, a liquid-like density and a high level of diffusion, sc-CO_2 treatment is well-known and particularly developed in the industrial sector [12]. The sc-CO_2 can be used as solvent for dry cleaning and for extraction for instance. For textile treatments, sc-CO_2 have been applied on natural fibres such as cotton and showed a degradation of the tensile strength

at 160°C and 300 bar [13]. It was gaining popularity among coffee manufacturers looking to remove the caffeine. In more recent applications, this treatment has been employed to extract 2,4,6-trichloroanisole from cork stoppers, responsible for the "corked" taste that spoils wines [14].

To the best of the author's knowledge, and on the basis of this open bibliography, it appears that this process, quite extensively studied and used for the lignocellulosic fractionation pretreatment for biorefinery [15] or for molecule extraction [6-7], was rarely envisioned and used for the preparation and treatment of plant fibres for material applications. Only Guttiérrez et al. [18] studied the effect of sc-CO_2 treatment on Curauá fibre properties (*Ananas lucidus*). Their results exhibit a partial extraction of lignin and a fibrillation of the fibres induced by sc-CO_2 treatment. Recently, a Chinese research team filed a patent describing a treatment for hemp fibres combining sc-CO_2 and conventional chemical treatments [19]. The patent describes a degumming method of hemp fibres that can significantly reduce lignin and other non-cellulosic components and more generally improve processing and quality of hemp fibre products. These preliminary results showed that the treatment of plant fibres with supercritical CO_2 deserved to be deepened. So, the aim of this present work was to evaluate the potentialities and impacts of such a treatment for the preparation of hemp fibres for composite applications. It involves various and complementary analysis techniques taking into account several physicochemical parameters. Two treatments involving two distinct sets of pressure and temperature, and located in the supercritical area of CO_2 have been investigated and compared. The first one, **TF-1,** is performed at 40°C and 75 bar (just above the critical point), and the second, more severe, **TF-2,** is carried out at 129°C and 149 bar. The influence of these treatments was evaluated by the examination of the biochemical, physical and mechanical properties of the fibres.

2. Materials and methods

2.1 Plant materials

Hemp fibres (*Cannabis sativa* L., cultivars 'Fedora 17') used to conduct this study came from the same batch as was used in Placet et al. [20]. They were cut and harvested in September 2013. These operations were carried out on a short time with the objective of minimizing the retting phase. The straws were then processed using an industrial process that includes breaking and scutching of the stalks. The extracted raw fibres were

delivered in a disordered form which contains both single and technical hemp fibres with a very low content of shives.

2.2 sc-CO_2 treatment

The sc-CO_2 treatment process was carried out using a home-made batch reactor in stainless steel manufactured in Dijon, France. This reactor, with a total capacity of 100 cm^3, has a closure system using six screws and is equipped with a Teflon seal ensuring leak tightness. It has an upper limit of 250 bar overpressure.

Hemp fibres were subjected to two types of sc-CO_2 treatments. The first one, named **TF-1** is performed at 40°C under a pressure of 75 bar, so just above the critical point in the supercritical state. The second one, **TF-2** is carried out under high temperature and pressure conditions (129°C – 149 bar). Technical fibres were first placed in the reactor and then conditioned under vacuum during 4 hours. The system was then filled with argon gas in order to keep the fibres under inert atmosphere and to purge the injector prior to introducing CO_2. The reactor was placed in ice bath so that sufficient amount of CO_2 was supplied for the experiment. The amount of CO_2 injected in the reactor was measured and controlled using a balance. The reactor, containing fibres and CO_2 was equipped with a heating sleeve whose temperature program was registered using the software LabVIEW®. When the set temperature was reached, the experiment began and lasted 17 hours. After that, the reactor was promptly depressurized to allow its opening and characterization of fibres. The quantity of hemp fibres introduced within the reactor was about 70-80 mg for each test. The parameters used for each test are described in Fig. 1.

Figure 1 Phase diagram of CO_2 and parameters for the two types of treatment

	TF-1	TF-2
Temperature (°C)	40	129
Pressure (bar)	75	149
Mass of CO_2 (g)	33	34
Mass of fibres (g)	3.8	3.8
Duration (h)	17	17

2.3 Fibre characterization techniques

2.3.1 Scanning electron microscopy (SEM)

Observations of treated and untreated hemp fibres were realized on Hitachi VP-SEM SU1510 equipment (Hitachi High Technologies America). The back-scattered electrons (BSE) imaging mode was used to obtain the images. The images were saved with magnification ×500, acceleration voltage of 15 kV and vacuum pressure equals to 30 Pa.

2.3.2 Thermogravimetric analyses

Thermogravimetric analyses were performed on a TA Instruments TGA Q600 thermoanalyzer using platinum pans. Samples (5–10 mg) were heated from room temperature to 800 °C at a rate of 20 °C.min^{-1} under air flow (100 mL.min^{-1}). Weight loss percentages were recorded using the TA Universal Analysis 2000 software.

2.3.3 Bio-chemical analyses

Prior to lignin and carbohydrate content determinations, sc-CO_2 treated technical fibres (**TF-1** and **TF-2**) and non-treated fibres (**NTF**) were powdered for the purpose of sample homogenisation. Thus, 3 g of each sample type was cut with scissors and then milled in a centrifugal grinding mill (Retsch MM2000 Mill). The lignin contents were determined using the Klason method well detailed in [20]. Carbohydrate identification and quantification were performed using HPAEC (ICS-5000+ DC, Dionex) following a

procedure fully described in [20]. Analyses were performed in three independent assays for **TF-1**, **TF-2** and **NTF**.

2.3.4 Water uptake

The water vapour sorption isotherms were measured using to the Dynamic Vapour Sorption (DVS) technique. The equipment (Surface Measurement Systems) used for these studies measures the uptake and loss of water gravimetrically using a microbalance (Cahn) with a mass resolution of ±0.001 mg. The partial pressure of water vapour around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The samples, each weighing between 6 and 8 mg, were equilibrated under various humidity environments, from 0% to 90% of relative humidity (RH) in air-tight containers. After a decrease to the dried state (0% RH), the RH was increased incrementally by steps of 2% RH from 0 to 10% RH, and by steps of 10% RH from 10% to 90% RH. It was then reduced again incrementally to 0% RH by steps of 15% RH. The temperature (20°C) was kept constant during the entire experiment. The first conditioning step with an equilibrium at 0% RH (120 min at 40°C and 180 min at 20°C) ensures similar conditioning for each batch of analysed fibres. For each RH step, a dwell at RH was maintained during 3 hours, except for the last one (90 % RH) which lasted 5 hours. These times were determined using preliminary experiments. They represent the time necessary to reach the moisture equilibrium (characterised by a variation of the mass lower than 0.003% on a time interval of one minute). The running time, target RH, actual RH and sample weight were continuously recorded with a sampling rate of 0.05 Hz. The water content is defined as the fraction determined by dividing the mass of water that fibres contain by the fibre dry mass. The adsorption behaviour of hemp fibres was analysed by fitting experimental data with the Hailwood Horrobin (H-H) model [21] based on Equation 1.

$$\frac{H}{M} = A + BH - CH^2 \qquad\qquad (1)$$

Where M is the moisture content at a given percentage of relative humidity H. A, B and C are constants. It is also possible to calculate equilibrium constants (K_1 and K_2) and molecular weight of cell wall polymer per sorption site (W) using these parameters which are estimated by minimization algorithms. The M0 parameter, equal to 1800/W, was also calculated.

2.3.5 Tensile characterization on hemp fibres

Some fibres (single fibres and possibly small bundles of fibres) taken from the disordered raw technical fibres were tensile tested before and after treatment. Approximately 40 fibres with a mean diameter of about 20 μm were tested following the procedure fully described in [20], except for the crosshead displacement rate and the controlled relative humidity that were set at 10 μm.s^{-1} and of 32 % ± 3% in this study. Considering the dependence of the tensile strength and stiffness of hemp fibres on their diameter [22], and to ensure a meaningful comparison, tests were performed on elementary fibres having an average diameter of approximately 20 μm. The mean value and standard deviation of these tensile properties were computed for each batch of fibres. A statistical analysis was also performed using EasyFit®. The best distribution function for each property was identified using Anderson-Darling criterion. The Young's modulus and the ultimate strength are described with a lognormal (LogN(μ, λ)) distribution and the strain at failure is defined by a Weibull (Weibull(α, β)) distribution (Eqs. 1, 2).

$$LogN(\mu, \lambda) : f(x) = \frac{1}{x} \frac{1}{\lambda \sqrt{2\pi}} \qquad (2)$$

$$Weibull(\alpha, \beta) : f(x) = 1 - e^{-\left(\frac{x}{\beta}\right)^{\alpha}} \qquad (3)$$

2.3.6 Fibre fineness

The fibre width distribution for each batch was measured via an automated apparatus MorFi (Techpap, Grenoble, France). The protocol used to do these measurements is fully described in [20]. Over 2,000 fibre elements were measured for each batch.

2.3.7 Powder X-ray diffraction (XRD)

The **NTF** and **TF-2** samples were analysed using X-ray diffraction according to the same procedure as the one fully described in [20]. The amount of crystalline cellulose was determined using the Rietveld method.

2.3.8 Analysis of VOCs by SPME and GC-MS

Solid phase microextraction (SPME) was used to analyse the volatile organic compounds (VOCs) extracted from the treatment of the hemp fibres with sc-CO_2. A silica-based SPME fibre coated with divinylbenzene/carboxen/plydimethylsiloxane (DVB/CAR/PDMS, 50/30 lm, Stableflex) from Supelco to adsorb VOCs extracted during sc-CO_2 treatment VOCs present on SPME fiber were analyzed in gas chromatography coupled to a mass spectrometer (GC-MS).

3. Results

3.1 Fibre surface morphology

SEM images (Fig. 2) indicate an effect of sc-CO_2 treatment at the microscopic scale. The image at the left of the Fig. 2 shows a strong surface roughness and a lot of pectic residues and impurities on the surface of the untreated hemp fibre bundles while the image at the right reveals clean fibres with very few residual impurities. The sc-CO_2 treatment also makes the cellulose macrofibrils apparent. Thus, the treatment seems to improve the individualisation of the fibres within the same bundle.
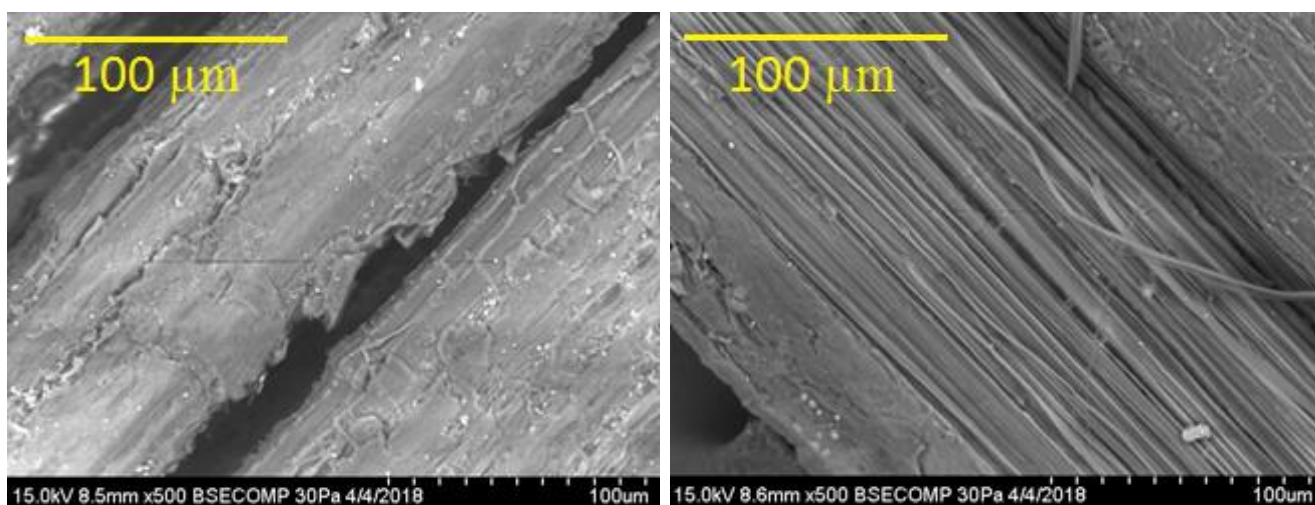

Figure 2 SEM images of **NTF** (left) and **TF-2** (right)

3.2 Fibre fineness

The impact of the sc-CO_2 treatment on the fibre fineness was quantified by measuring the width of the fibre elements in both batches, **TF-1** and **TF-2**. These results were then compared with those obtained on non-treated fibres (**NTF**) and for which the results were previously published in [20]. The fibres treated in this work were taken in the same

batch than the fibres tested and characterised in [20]. Fig. 3 shows the histogram distribution of the fibre width for each batch. For **NTF**, we observed a monomodal distribution of fibres' width centred on the intervals 53-69 μm. In contrast, results from **TF**-1 and **TF-2** revealed a bimodal distribution. It is characterized by the presence of two main populations. The first population was defined with an average width of 5-21 μm and the second one was around 70 μm. We observed a significant decrease in the average width of fibre elements using the sc-CO_2 treatment. In fact, the average width is 56.2 ± 1.5 μm for **NTF**, 35.8 ± 1.6 μm for **TF-1** and 33.6 ± 3.7 μm for **TF-2**. The typical width ranged between 5 and 150 μm and a lognormal distribution offered the more realistic fit to the width measurements. A general shift of the distribution of the **TF-1** and **TF-2** widths to the left (to the smaller diameters) compared to the **NTF** can be observed. For **NTF**, 26.5% of the elements have a diameter between 5 and 37 μm, whereas 37.6% and 43% for **TF-1** and **TF-2** respectively. This width range represents the typical elementary primary hemp fibres. Regarding the different types of treatment, no significant difference can be observed between both treated fibre batches in the selected pressure and temperature conditions.
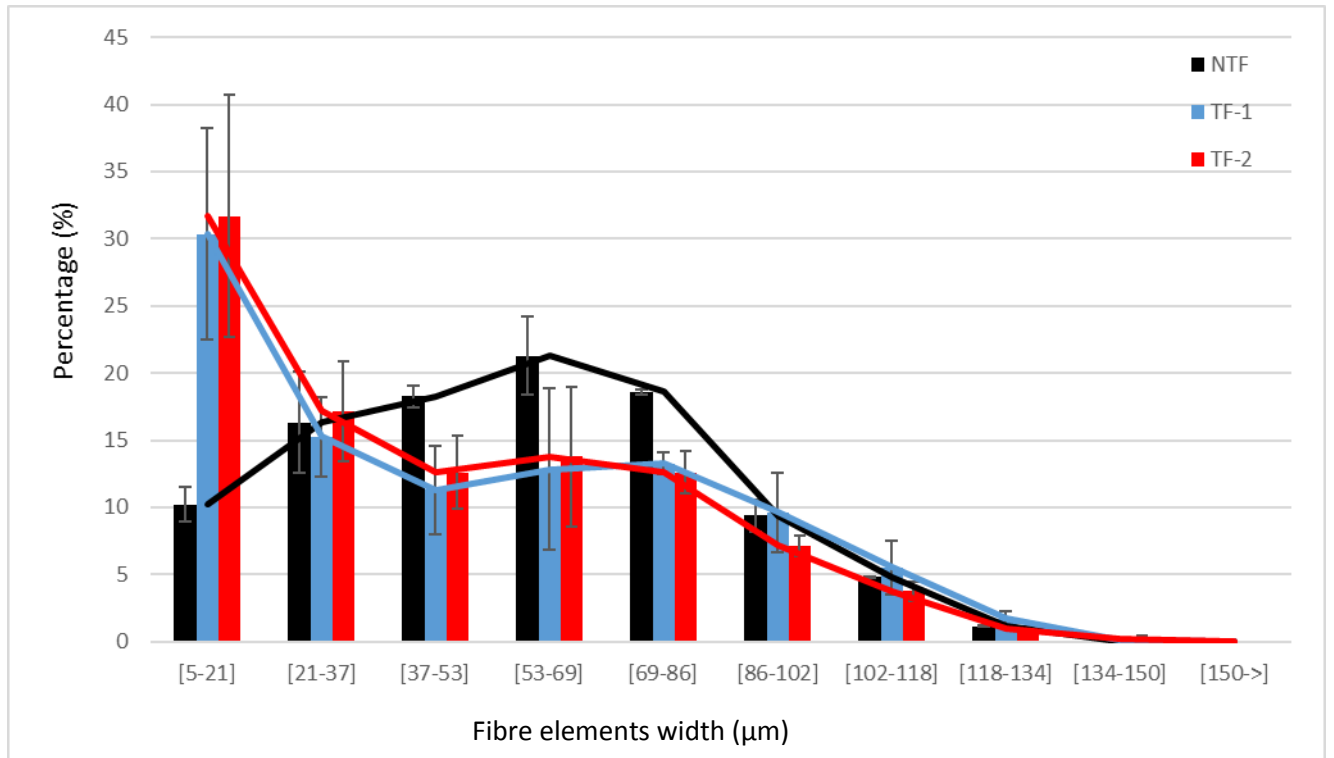

Figure 3 Histogram distribution of **NTF**, **TF-1** and **TF-2** samples' diameters

3.3 Thermal properties

The influence of the sc-CO_2 treatment on the thermal properties of the fibres was also investigated using thermogravimetric analysis. Samples from each batch (**NTF**, **TF-1** and **TF-2**) were characterized. The thermograms represent the weight loss of the fibres as a function of increasing temperature (Fig. 4). As already depicted in the literature, the obtained curves show three stages. The first one exhibits a peak around 60°C that corresponds to the evaporation of the water (DTGA curves). The second stage is generally attributed to the degradation of the majority of hemicelluloses, celluloses and pectin degrade between 200°C and 400°C. The third peak (around 450°C) is characteristic of the degradation of the lignin and of the degradation of the formed by-products [23]. The results showed that the treatment with sc-CO_2 does not induce significant variations on the thermal degradation profiles, except for the third peak on the DTG curve. A decrease is observed for **TF-1** and **TF-2** compared with **NTF**. This result, in agreement with the results obtained by Gutiérrez et al. [18] on curaua fibres, can be attributed to the partial extraction of lignin from fibres during the sc-CO_2 treatment.
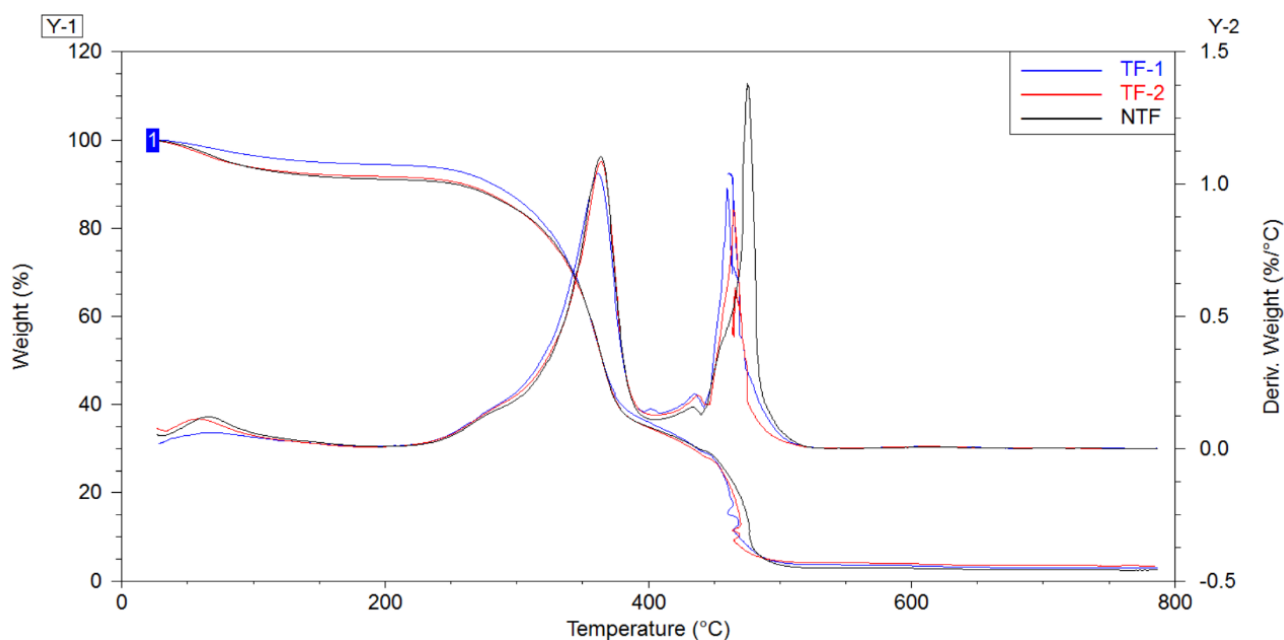

Figure 4 TGA thermograms and DTG curves of hemp fibres before (**NTF**) and after sc-CO_2 treatment (**TF-1** and **TF-2**).

3.4 Tensile properties

The mechanical properties of the fibres from **NTF**, **TF-1** and **TF-2** were evaluated by tensile tests at a temperature of 20°C and 32% of relative humidity. The average tensile properties and their standard deviations are shown in Tab. 1. Their statistical distributions (Fig. 5) lead to an accurate assessment of the effect of the treatment on the tensile properties. The experimental data were correctly represented by Lognormal and Weibull distributions. For **NTF**, the average apparent tangent modulus was equal to approximately 19 GPa, 374 MPa for the tensile strength and 2.5% for the strain at failure. These values were on the same order of magnitude of those already reported in the literature, considering the same range of fibre diameter [20]. When compared to the properties of **NTF**, it can be concluded that the treatment induces a significant decrease in the tensile properties. A loss of approximately 43% and 30% are measured on the rigidity, for **TF-1** and **TF-2** respectively, as well as a loss of 47% and 40% in strength, 19% and 16% in strain at failure. It can also be underlined that the second treatment (**TF-2**) which is more aggressive than the first one, does not result in a more marked decrease in tensile properties. Further studies would be useful to refine the potential relationship between the process parameters and the resulting tensile properties.

It has also to be underlined that the fibres tested in the three batches were selected in a narrow diameter range (mean diameter of approximately 20 µm) to avoid any diameter effect in the comparison of the results. Taking into account the effect of the treatment on the fibre fineness, it is probable that a sampling representative of the diameter range of the different batches would have resulted in a different conclusion.

Table 1 Tensile properties of CO_2 treated hemp fibres

Tensile properties	NTF		TF-1		TF-2	
	Mean ± SD Min…Max	Distribution Law	Mean ± SD Min…Max	Distribution Law	Mean ± SD Min…Max	Distribution Law
E (GPa)	19.2 ± 12.9 3.5…58.3	LogN (µ, λ) 2.74, 0.67	11.0 ± 6.9 0.7…35.5	LogN (µ, λ) 2.16, 0.76	13.5 ± 8.9 1.1…41.3	LogN (µ, λ) 2.35, 0.77
σ_R (MPa)	374 ± 215 77…934	LogN (µ, λ) 5.75, 0.62	197 ± 93 60…470	LogN (µ, λ) 5.18, 0.44	226 ± 155 57…752	LogN (µ, λ) 5.23, 0.61
ε_R (%)	2.51 ± 1.20	Weibull (α, β)	2.03 ± 1.39	Weibull (α, β)	2.12 ± 1.00	Weibull (α, β)

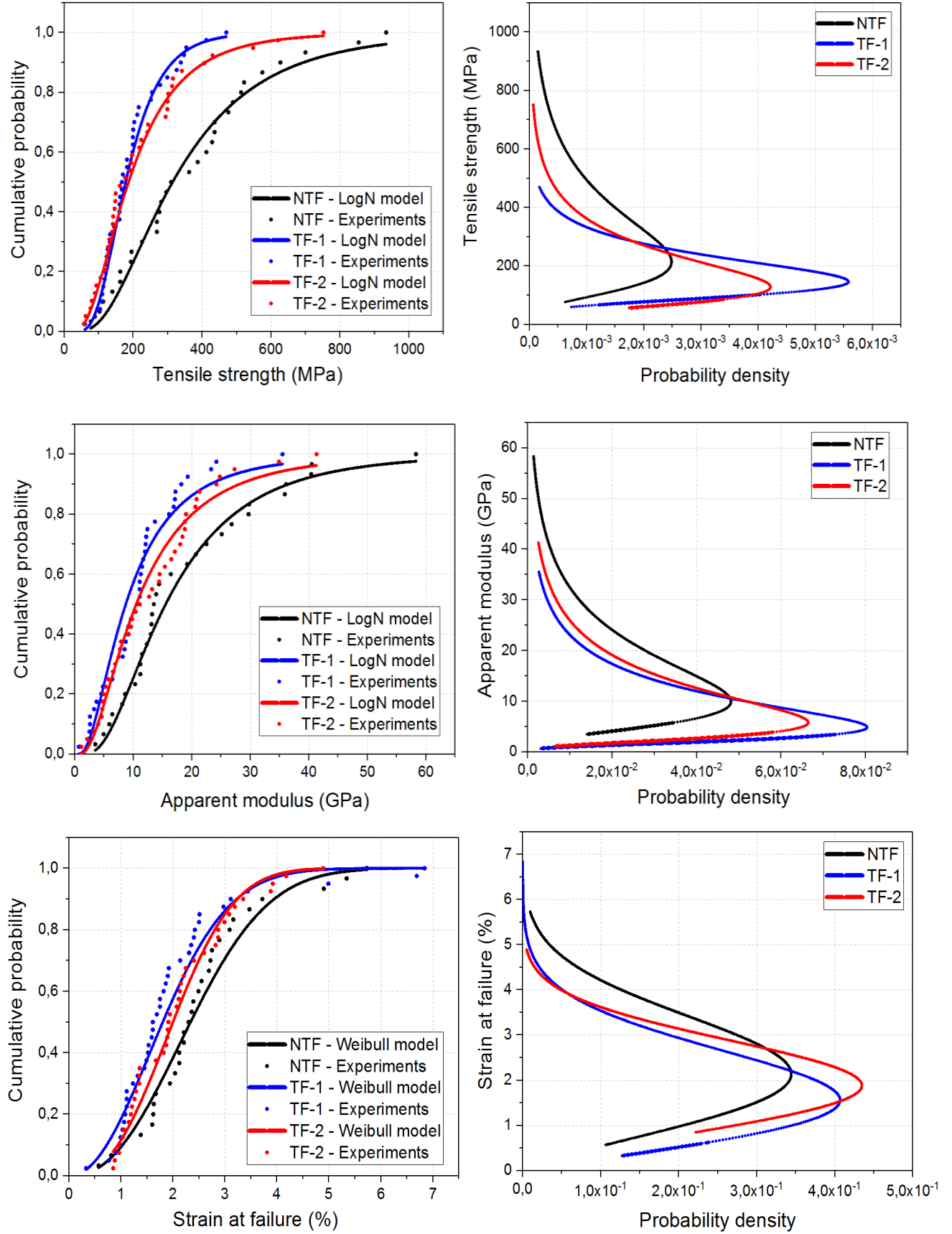|	0.57…5.73	2.29, 2.74	0.33…6.84	2.04, 2.15	0.85…4.89	2.49, 2.32
Diameter (µm)	20.87 ± 8.25	/	20.48 ± 5.49	/	19.87 ± 4.96	/

Figure 5 Probability density and cumulative distribution functions of the tensile properties

3.5 Hygroscopic behaviour of fibres

The water vapour sorption isotherms of the fibre samples **NTF**, **TF-1** and **TF-2** are presented in Fig. 6. As already noted in the literature, the adsorption and desorption curves have a hysteretic behaviour and a sigmoid shape [21]. This nonlinearity results from the combination of different sorption mechanisms. The first zone (0-15% RH) corresponds to the adsorption of a molecular monolayer. The second zone (15-70% RH) refers to the adsorption of molecular multilayers and the third domain (70-100% RH) is generally attributed to capillary condensation.
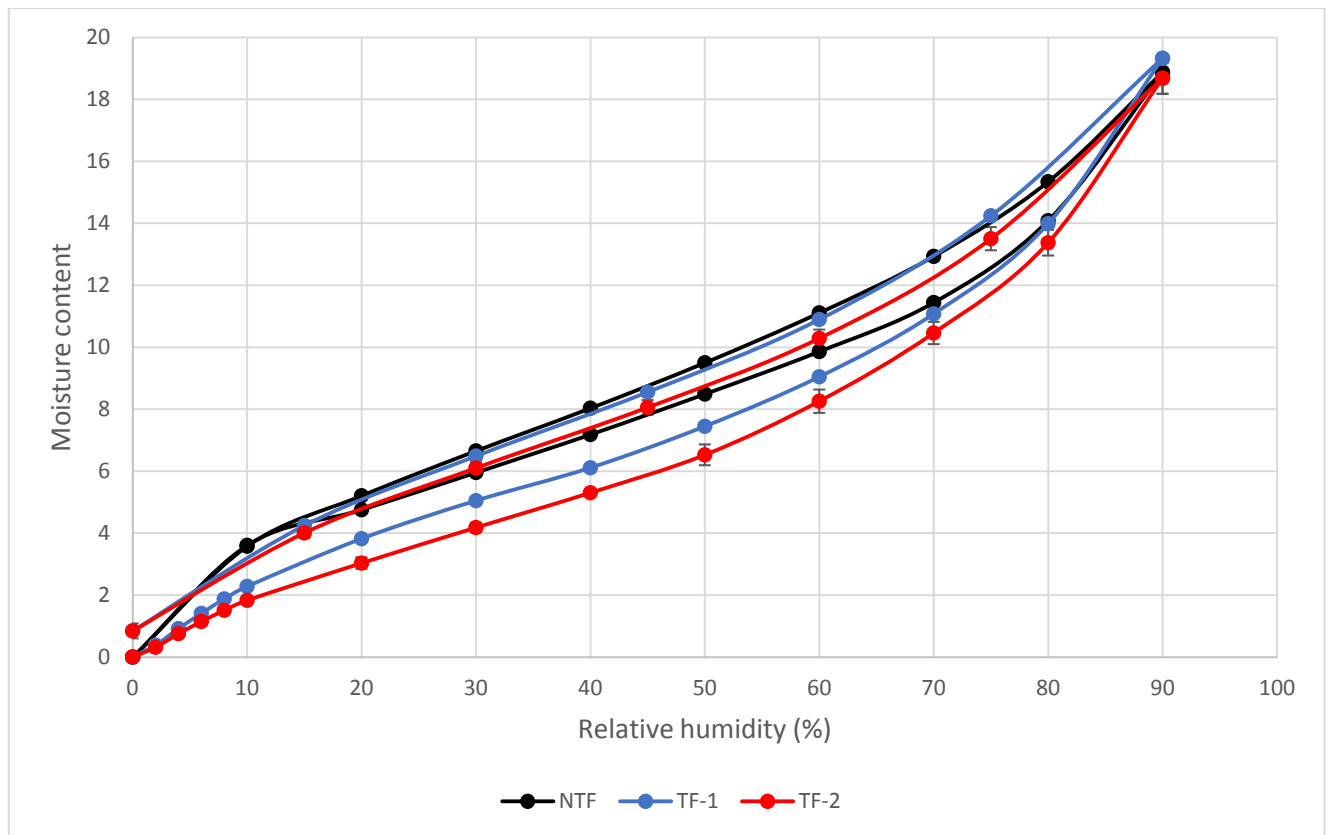

Figure 6 Water vapour sorption and desorption isotherms

A down shift of the isotherms of **TF-1** and **TF-2** compared with **NTF** was observed. At 50% RH during the absorption, there was a 13% and 24% decline in the equilibrium moisture content (EMC) when compared to **NTF**, for **TF-1** and **TF-2** respectively. At 50% RH, the significant decrease in EMC for **TF-2** is greater than the one measured on flax fibres treated under autoclave [24], for example. It illustrates the good efficiency of

the sc-CO$_2$ treatment to alleviate the hygroscopic capacity of hemp fibres when compared to other treatment processes proposed in literature. The reduction of the moisture sensitivity of the treated fibres reflects a decrease in the available hydroxyl groups at their surface and in their wall. This decrease was quantified using the Hailwood Horrobin model (HH model) [25]. The experimental sorption isotherm curves were fitted using the HH model and the parameter values identified by inverse method (minimizing algorithm). The identified values are presented in Tab. 2. The difference between treated and non-treated fibres is mainly on the K$_1$ equilibria constant and M$_0$ parameter. K$_1$ is the constant between hydrate and dissolved water. M$_0$ is a specific property related to the moisture sorption of the materials. It indicates the MC corresponding to all available sorption sites totally occupied by water molecules in the monolayer [26]. A decrease of 6.6% and 10.3% of M$_0$ is observed compared to **NTF**, for **TF-1** and **TF-2** respectively. This is directly attributed to the reduction of the number of available hydroxyl groups.

Table 2 Hailwood Horrobin fitting parameters

HH parameters	A	B	C	K1	K2	W	M$_0$ (1800/W)
NTF	1.597	0.1619	0.00141	13.58	0.806	337.8	5.33
TF-1	2.960	0.1516	0.00146	7.17	0.830	361.3	4.98
TF-2	4.468	0.134	0.00145	4.56	0.844	376.6	4.78

The moisture absorption curves (moisture content as a function of time) were also plotted and analysed. Fig. 7 presents the absorption curves recorded when the fibres were exposed to a change in RH from 10 to 20%, 40 to 50% and 60 to 70% RH, respectively. When compared to the sorption isotherms which give information on EMC, the moisture absorption curves provide more information related to the sorption and diffusion kinetics. At 20% RH, the moisture uptake of **NTF** is largely higher than the one for **TF-1** and **TF-2**. A slight delaying effect is also observed. When vapour concentration increases (for RH above 70%), the treated fibres batches absorbed as high or higher water content than **NTF**. In this zone (70-100 RH), water molecules form clusters of large sizes and capillary condensation can occur. For treated fibres, the extraction of polysaccharides and lignin can increase the distance between the chains

within the cell wall, and thus increase the void volume content. It could facilitate the water clustering and capillary condensation.
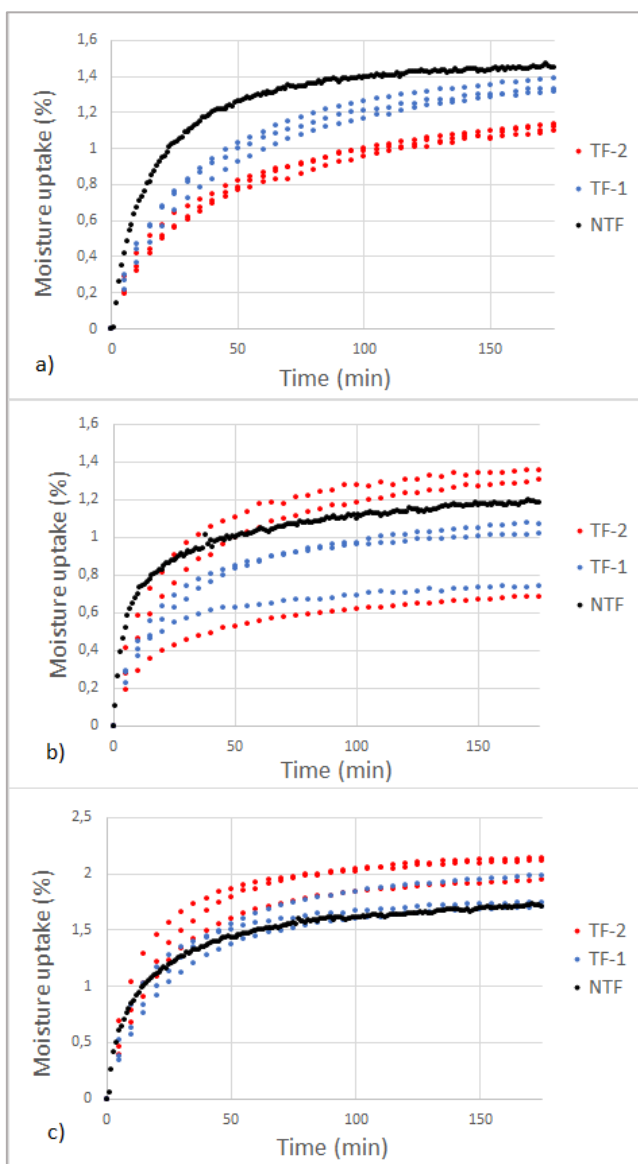

Figure 7 Sorption kinetics profile for **NTF**, **TF-1** and **TF-2**. a) 10-20% RH, b) 40-50% RH and c) 60-70% RH

3.6 Chemical composition and ultrastructure analysis

The chemical composition of treated and non-treated hemp fibres analysed herein, is presented in Fig. 8 and Tab. 3 Total carbohydrate and Klason lignin contents were determined (Tab. 3). The **NTF** batch contained 80.9% of carbohydrates and 4.9% of

Klason lignin as relative percentage of dry matter. These values agreed with those given by the literature [3].

Table 3 Carbohydrate and Klason lignin contents of the fibres expressed as percentage of dry matter

	NTF	TF-1	TF-2
Total carbohydrate content	80.9 ± 0.5	78.9 ± 0.7	75.0 ± 3.9
Klason Lignin	4.90 ± 0.2	3.97 ± 0.11	3.70 ± 0.02

The sc-CO_2 treatment affected the chemical composition of fibres. Indeed, the variation of total carbohydrate content between the batches **NTF**/**TF-1** and **NTF**/**TF-2** suffered a decrease of 2.5% and 7.3% respectively. Regarding Klason lignin relative content, we noticed a reduction of 19% and 24.5% for **TF-1** and **TF-2** respectively, compared with **NTF**. The variations are only statistically significant for the lignin content. Statistical tests indicated a P value higher than 0.05 for all the comparisons between the different batches except for the correlation of the lignin content between **NTF** and **TF-2** characterized by a P value equal to 0.03. The total carbohydrate content was not the most useful indicator therefore the content of monosaccharides (fucose, arabinose, rhamnose, galactose, xylose, mannose, galacturonic acid, glucuronic acid, glucose) was also quantified (Fig. 8). The major monosaccharide contained in hemp fibres was glucose (Glc). Glucose and cellulose are often wrongly assimilated. The other minor monosaccharides (with respect to mass) are related to pectins and hemicelluloses. The proportion of each type of carbohydrate declined with the sc-CO_2 treatment but at different rates. The three monosaccharides whose changes in relative content were the most important (around 30% of decrease) were rhamnose (Rha), galacturonique acid (GalA) and xylose (Xyl). Rha and GalA are the main component of pectin, whereas Xyl is generally associated to hemicellulose. The sc-CO_2 treatment predominately extracted lignin, hemicellulose and pectin. Except carbohydrates, lignin and water, hemp fibres are composed of other non-quantified products. There are lipid compounds, proteins and minerals. It is not possible to evaluate easily the effect of the treatment on these components. However, the C/N (Carbon/Nitrogen) ratio provides part of the answer concerning the variation of proteins content. It was not subject to significant variation since it was equal to 120 for **NTF**, 129 for **TF-1** and 127 for **TF-2**. So, proteins were

not significantly affected by the sc-CO$_2$ process. Furthermore, as this work reported a decrease of the proportion of carbohydrates and Klason lignin content, a possible explanation for the remaining proportion of the fibres' components is that it corresponds to non-quantified compounds such as lipids, proteins and minerals.
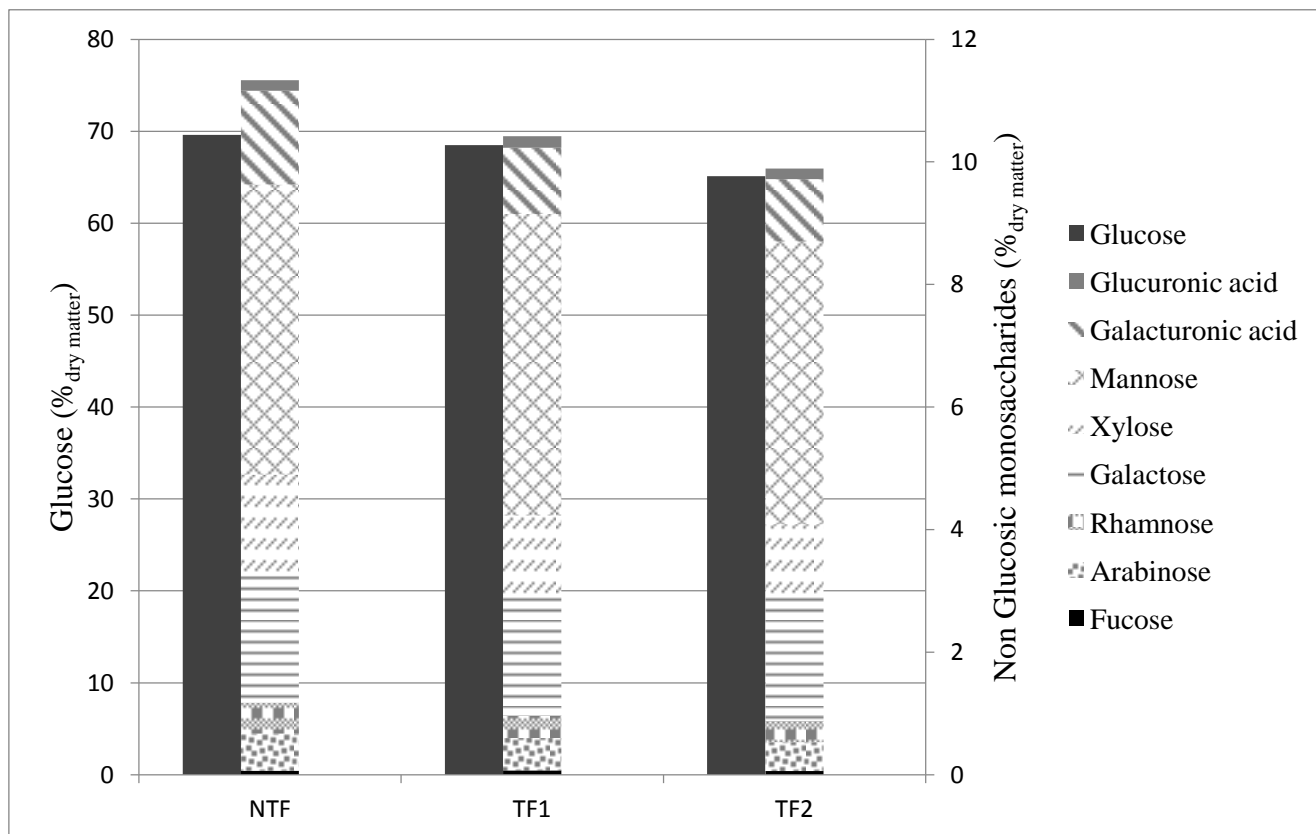

Figure 8 Relative contents of monosaccharides in treated and non-treated fibres. Fuc fucose, Ara arabinose, Rha rhamnose, Gal galactose, Xyl xylose, Man mannose, GalA galacturonic acid, GlcA glucuronic acid, Glu glucose

The results from the XRD analysis revealed a slight decrease of the crystalline part of the cellulose from 78.8% for **NTF** to 76.8% for **TF-2**. These orders of magnitude are in good accordance with values reported in the literature for hemp fibres ranging from 60% to 88% [20, 27].

3.7 Analysis of VOCs by SPME-GC-MS

The gas sample analysed when relieving pressure of the reactor highlighted the presence of fatty acids, identified as *n*-hexadecanoic acid and *n*-decanoic acid, with a probability of 83% and 77%, respectively.

4. Discussion

The results described above reveal three major effects of the sc-CO_2 treatment on hemp fibres.

The first is the significant increase in the fibre fineness and cleanness. The sc-CO_2 treatment promotes clearly the inter-fibre decohesion and thus the separation of the individual fibres within the technical fibres. Indeed, the morphological analysis indicated a higher proportion of fibres whose diameter was between 5 μm and 21 μm (corresponding to single primary or secondary fibres or bundles of secondary fibres). This is mainly explained by the extraction of the substances responsible for the cohesion of single fibres together, i.e, pectins (present in the middle lamella) and lignin.

The second major result is the reduction of the moisture sensitivity. The sc-CO_2 treatment induces a significant decrease in the EMC and also a slowdown of moisture diffusion when fibres are exposed to RH inferior to 70%. This decrease in moisture absorption is also directly linked to the modification of the biochemical composition and organisation of the fibre wall. Polysaccharides such as hemicellulose and pectin within the fibre wall possess numerous hydroxyl groups, which impart predominantly to the fibre its hydrophilic character. Chemical analysis showed a decrease of the monosaccharides GalA, Rha and Xyl, that are the main components of pectin and hemicellulose, after the sc-CO_2 treatment. The process was able to extract enough carbohydrates to make hemp fibres less sensitive to moisture, in particular in the sorption domain dominated by bound water (i.e. for RH inferior to 70%). The sc-CO_2 induces a decrease in the number of available hydroxyl groups, which naturally diminish the monolayer water content. On the contrary, the changes in the polysaccharide structure and organisation and the possible increase in void volume result in a similar and even increased of the EMC in the third zone of the sorption isotherm (for RH above 70%).

These properties enhancement (fibre individualisation, cleanness and moisture sensitivity reduction) were obtained while retaining a same thermal resistance. This later is an important issue, in particular when considering the composite manufacturing temperatures used for most of the current organic matrices (with a temperature ranging generally from 100°C to 200°C).

In contrast, the last significant effect is quite more negative. A significant decrease in the fibre rigidity as well as a more brittle fracture were pointed out for treated fibres when compared to **NTF**. This loss in tensile properties can be explained by the slight disordering of cellulose (revealed by the slight decrease in crystallinity index) and the partial degradation of hemicellulose and pectin, which certainly play a role in the architecture of the cell wall. Although no defects on the external surface of fibres were observed on SEM images, it can also be hypothesised that the treatment, and more exactly the depressurization step and the potential associated shock, induces defects and/or porosities within the fibre cell wall. These defects could explain the strong decrease in tensile strength and are consistent with the increase in EMC observed when exceeding 70% RH. Interestingly, despite a more significant removal of constituents, the second treatment (**TF-2**) did not result in a more marked decrease in tensile properties. Thus, the decrease in tensile properties could be mainly driven by the induced physical effect rather than by the change in biochemical composition.

Therefore, even if the sc-CO_2 treatment implies positive effects on hemp fibres in view of their embedment in polymeric matrices as above mentioned, it also induces a decrease in tensile strength and stiffness comprised between 30 and 50% for the considered treatment parameters. This could have a substantially impact on the mechanical properties resulting at the composite scale.

So, the sc-CO_2 fibre treatment still need to be optimised to tune its effect on these main inputs (fineness, cleanness, moisture sensitivity and tensile properties). Anyway, it is already a relevant option for composite families for which the aspect ratio is prevalent on the fibre tensile performance (such for short-fibre composites). As a matter of fact, some works pointed out that even if the treatment used to separate the fibres reduces the tensile properties of the fibres themselves, a significant increase in the properties at the composite scale can be observed thanks to the better individualisation of the fibres and also to a better cohesion at the fibre/matrix interface [28].

5. Conclusions

A sc-CO_2 treatment was performed on industrial hemp fibres and some of their properties were significantly modified. This innovative "green" process allowed the improvement of the fibre cleaning and refinement and the decrease of their moisture sensitivity, while retaining their thermal resistance. All these property modifications are strongly related to the extraction of polysaccharides and lignin. In the meantime, it also

induces a decrease in the tensile rigidity of the fibre as well as a more brittle fracture. However, this variation does not compromise the use of the treated fibres for the development of composites. The benefits in terms of fibres fineness and moisture sensitivity are results in favour of the use of the sc-CO_2 treatment for composites applications, whereas the decrease of the mechanical properties is a real hurdle to the development of treated hemp fibre composites. This sc-CO_2 process may be extended to different plant fibres. The treatment conditions herein reported have also to be optimized in order to improve the properties of the fibres and current works are focused on the characterization of fibre/matrix interface.

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