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## Original Article

# Mechanical behavior of chemically-treated hemp fibers reinforced composites subjected to moisture absorption



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## ABSTRACT

Natural Fibers Reinforced Composites (NFRC) are finding much interest as substitutes for glass- or carbon-reinforced composites thanks to their lightness, easy handling, processing and recyclability. However, their polarity makes them incompatible with hydrophobic thermoplastic matrices, leading to extended moisture adsorption which causes the debonding between fibers and matrix, affecting, thus, the mechanical properties of NFRCs. In the present work, NFRCs were manufactured using hemp fibers previously chemically treated with NaOH alkali solutions or (3-Glycidioxypropyl) trimethoxysilane (GPTMS) solutions of various concentrations. To assess the effectiveness of the used chemical treatments in hindering the moisture adsorption and the entailed mechanical failure of the NFRCs, untreated and treated hemp fibers based composites were subjected to moisture adsorption test and then to tensile testing as a function of the chemical treatment, temperature and concentration of reagents. The results show that the treatments with 5 wt% of both NaOH and GPTMS are the most effective, reducing composites' water uptake from 7.74% to 6.46% and 5.58% respectively at room temperature, and from 9.67% to 8.19% and 8.13% respectively at 50 °C. Moreover, the comparison between the mechanical testing results carried out before and after the moisture adsorption test, shows that the water uptake induces mainly a stiffness decrease (about 50% when alkali treatments were used and about 60% using silane treatment), while not significantly affect the loading capability of the composites regardless of chemical treatment. However, the specimen obtained using 5 wt% GPTMS is more effective in the prevent the failure of the composite induced by water uptake.

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## 1. Introduction

A natural fiber-reinforced composite (NFRC) consists of a polymer matrix incorporated with natural fibers as reinforcement [1]. Natural fibers are obtained from plants or animals. Their use has been proposed in the development of alternative composites as an environmentally friendly substitute for synthetic fibers in the reinforcement of polymer matrices [2–7], cementitious materials, such as mortars and concretes [8–12] and sandy soil [13]. Particularly, the NFRCs have been widely proposed in various application fields, such as aerospace, automotive, marine, infrastructure, military and aircraft [1]. The growing interest in natural fibers as reinforcement in polymer-based composites is due to their low density, which confers lightness for the obtained structures, high toughness and strength, easy handling and processing, recyclability and good thermal and acoustic insulation [14,15]. Moreover, they are non-toxic and supplied by renewable, continuous and abundant raw materials [15]. The physical properties of the natural fibers, and therefore of the NFRCs, are ascribable to their chemical composition and particularly to the presence of cellulose, hemicelluloses and lignin which are the basic components of these fibers.

Despite their remarkable advantages compared to glass or carbon-reinforced composites, NFRCs have also several drawbacks that limit their employment. These disadvantages can be mainly attributed to the hydrophilic nature and high permeability of the natural fibers [1]. Carvalho et al. [16] reported that macambira fibers reinforced polyester composites adsorbed a higher amount of water than the fiber-free polyester matrix. The high moisture and water uptake as well as the low adhesion between fibers and polymer matrix are ascribable to the presence of hydroxyl groups in the structure of the fibers [17,18]. Water absorption is among the main causes leading to matrix cracking and dimensional instability, which in turn affect the mechanical properties of NFRCs and can result in NFRCs structure failure. The presence of water molecules at the fiber-matrix interface can be due to the diffusion of water molecules in the polymer matrix through micro-gaps between polymer chains, to the water capillary transport through defects and gaps in the matrix, or also to the water transport through the formation of microcracks caused by the fiber swelling following the water adsorption [19]. The onset of such phenomena is induced by the poor wettability between fiber and matrix [20]. The fiber-matrix adhesion plays an important role also in the transfer of stresses from matrix to fibers, which is one of the primary contributors towards the high mechanical properties of composites [21]. Poor surface adhesion is the principal reason for the formation of weak or ineffective interfaces between fibers and matrix [20].

Most studies have focused their attention on the development of various chemical treatment methods able to reduce the hydrophilic nature of different natural fibers (e.g. hemp [22–24], flax [25,26], sisal [27,28], kenaf [29,30], coir [31] and jute [32]), to improve both the adhesion of the fibers surface to the matrix [33] as well as to reduce moisture adsorption [17,18]. These chemical treatments generally involve alkaline, silane, benzoylation, acetylation, isocyanate, peroxide, and permanganate treatments [34–39].

Mwaikambo and Ansell [40] used the acetylation treatment on kapok, sisal, jute and hemp fibers obtaining the reduction of the water absorption through the decrease of the hydroxyl groups number. However, the most commonly used treatment to increase the long-term stability of NFRCs and to improve fiber-matrix interfacial bonding is the alkaline treatment. This treatment aims to eliminate the alkali-sensitive hydroxyl groups and to increase the fiber surface roughness leading to the fiber hydrophilicity decreasing and the improvement of the mechanical bonding respectively. The alkaline treatment can improve significantly several properties of composites such as tensile modulus and water absorption, as reported by Venkatesh et al. [41] and Bachtar et al. [42]. However, its effectiveness is strongly affected by both the concentration of the used solution and treatment duration. Kabir et al. [43] tested hemp fiber with NaOH solutions with different concentrations (0, 4, 6, 8, 10 wt%) for 3 h, proving that alkalization reduces the fibre strength, with 4% NaOH leading to the lowest value. The Authors ascribed this effect to the partial removal of hemicellulose and lignin. Their results are in agreement with those one reported by Sepe et al. [33] which used FTIR analysis to detect the reduction of hemicellulose and lignin in the fiber structure as a function of the NaOH concentration.

Prasad et al. [44] compared the effect of the treatments with 1% NaOH and 1% acrylic acid solution on banana fibers. Their results suggest that both treatments enhance mechanical properties and reduce the water absorption capacity of banana fibers. However, treatment with acrylic acid resulted in more effectiveness than NaOH. The improvement of the mechanical behavior and the decrease of the water uptake capability using treatments with NaOH and acrylic acid were obtained also by Vilay et al. [45] on bagasse fiber-based composites.

Another widely used treatment involves silanes acting as coupling agents. Silane treatment usually is carried out by immersing the fibers in a water/alcohol solution of a silane. The silane coupling agents are compounds with a silicon atom bonded to different functional groups able to chemically link the fiber surface and the matrix. The silane treatment enhances the degree of fiber-matrix adhesion and, thus, can lead to an increase in the strength and stiffness of the composites, as reported by Franco et al. [46,47]. Moreover, the bonding of the silane coupling agent to cellulose hydroxyl groups can entail the reduction of the number of the –OH groups exposed in the fiber-matrix interface also reducing the water uptake. Zahari et al. [48] showed that a silane treatment affects the water absorption of the black sugar palm-reinforced polypropylene composites. Treated fibers-based composites exhibited slightly lower water absorption compared to those made of untreated fibers. Liu et al. [49] studied the adsorption moisture behavior of the silane-treated corn stalk fibre-reinforced polymer composite obtained by fibers immersion in solutions with various concentrations of silane coupling agent (1, 5, 9 and 13 wt%). Among all the concentrations, 5 wt % of silane led to the minimum water absorption, showing that the water absorption increased using higher silane solution concentrations. Furthermore, the silane solution treatments of corn stalk fibre also reduce effectively the porosity of the polymer composite systems.

Dayo et al. [50] evaluated the effects of chemical treatments on the performances of hemp fibers by using

cyclohexane/ethanol, alkaline, and silane agents. The results of flexural, tensile and impact tests confirmed that the silane-treated fiber-based composites show the highest properties and the lowest water absorption.

Despite several studies that reported the effects of the chemical treatments on mechanical properties and water absorption ability of NFRCs, only a few works investigated their effect in the prevention of the composites' failure caused by the moisture uptake. Therefore, a comparative study, not present in literature until now as far as we know, has been conducted on woven hemp-reinforced composites aiming to investigate the relationship among the reagents used for the chemical treatment, their concentration, the modifications induced in the fibers structure and the moisture adsorption ability of the obtained composites, as well as their mechanical performance before and after the water uptake. The present study integrates and broadens the results reported in a previous work, where Sepe et al. [33] prepared the woven hemp-reinforced epoxy composites through a Vacuum Infusion Process (VIP) and investigated the effects of alkali and silane chemical treatments on the chemistry and morphology of the fibers, as well as on the tensile and flexural mechanical properties of the obtained laminates. To broaden knowledge about the relationship between the fibers chemical treatment and the properties of the woven hemp-reinforced epoxy composite, the present work investigates the composites absorption ability, according to ASTM D 570-98 standard method [51], as a function of the chemical treatment (alkali and silane treatments), the reagents concentration, temperature and the exposure time to water. Moreover, to evaluate the effect of the wet environment on the morphology of the samples, before and after the moisture absorption test, all composites were observed using Scanning Electron Microscopy (SEM). Then, the tensile strength and elastic modulus of composites were assessed through mechanical tests after the moisture absorption test to evaluate the ability of the chemical treatments to hinder the loss of mechanical strength caused by moisture exposition and leading to the failure of the composites. Finally, results obtained in the present work were cross-compared with those already available in Ref. [33] related to non-wetted materials to highlight differences.

## 2. Experimental methods

### 2.1. Materials

The PrimeTM 20LV epoxy resin, produced by Gurit, with a density of 1.084 g/cm<sup>3</sup> and a tensile strength of 73 MPa, was

selected as the polymer matrix and it was used in conjunction with a slow hardening agent. The matrix was reinforced using a woven hemp fabric with a simple weave, a count of 50 warp threads and 50 threads in the direction weft per inch, and with a weight of about 180 g/m<sup>2</sup>. Before preparing the composites, the woven hemp fabric surface was chemically treated. The used reagents were pellets of NaOH, pure Ethanol (98%) and (3-Glycidyloxypropyl) trimethoxysilane (GPTMS), all provided by Sigma Aldrich (Milan, Italy).

### 2.2. Woven hemp-reinforced epoxy composites preparation

The woven hemp fabric was cut into 280 × 220 mm × mm sheets with a weight of 11 g each. Afterwards, the surface of the natural fibers was modified, as reported elsewhere [33]. Briefly, two different chemical treatments were used: alkaline and silane treatments. The alkaline treatment was carried out using a solution of sodium hydroxide in water. The fibers were immersed in 1 wt% and 5 wt% water solutions of NaOH for 30 min. The ratio between the volumetric solution and the weight of the sheet was equal to 45 ml/g. Subsequently, the alkalinized fibers were rinsed several times with distilled water to allow for the removal of the sodium hydroxide residue. Finally, the cleaned fibers were dried in an oven at 70 °C for 24 h.

For the silane treatment, the GPTMS, with the chemical formula H<sub>2</sub>COCHCH<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, was used as a coupling agent. The GPTMS was previously pre-hydrolyzed at room temperature for 1 h in an 80/20 vol % solution of ethanol/water. Solutions containing 1, 5, and 20 wt% of GPTMS (weight of silane relative to the weight of hemp fabric) in ethanol/water mixture were prepared and the fibers were soaked within them for 1 h. The ratio between the volume solution and the weight of the sheet was fixed equal to 22.5 ml/g. After the treatment, the fibers were dried in an oven at 70 °C for 24 h.

The treated fabrics as well as an untreated fabric subjected only to drying in an oven at 70 °C for 24 h, were used to manufacture six different configurations of hemp/epoxy composites, labelled as reported in Table 1.

As a manufacturing process, a Vacuum Infusion Process (VIP) at room temperature was employed using a rectangular glass mold with sizes of 350 × 300 mm × mm [33]. Poly Vinyl Alcohol (PVA) was applied as a release agent on the mold surfaces. Four plies of textile were infused with a mixture of resin and hardener (100:26 wt ratio) previously prepared by mixing and degassing under vacuum. Afterwards, specimens were cured at room temperature for 24 h. Composites with 42% (±1) fiber weight fraction were produced (see Table 1).

**Table 1 – Composites Labels and features.**

Label	Fiber	Chemical treatment	Thickness $t_h$ [mm]	$W_f$ [%]	$V_f$ [%]
UT	Hemp	Untreated	1.36	42.9	34.5 (±1)
N1	Hemp	Alkaline treatment NaOH 1%	1.51	42.2	34.8 (±1)
N5	Hemp	Alkaline treatment NaOH 5%	1.68	41.9	33.9 (±1)
S1	Hemp	Silane treatment 1%	1.47	40.8	33.8 (±1)
S5	Hemp	Silane treatment 5%	1.46	42.0	34.7 (±1)
S20	Hemp	Silane treatment 20%	1.45	42.3	34.8 (±1)

Moreover, the total fiber volume fraction ( $V_f$ ) of all composites were reported in Table 1 and calculated as follows:

$$V_f = \frac{(W_f/\rho_f)}{(W_f/\rho_f) + (W_r/\rho_r)} \quad (1)$$

where  $W_f$  and  $\rho_f$  are the weights and density of the fibers respectively, whereas  $W_r$  and  $\rho_r$  are the weights and density of the resin respectively.

The water displacement method was used to measure the hemp density, recorded at 1.48 g/cm<sup>3</sup>, whereas the epoxy resin density was 1.084 g/cm<sup>3</sup>, as provided by the manufacturers' test report.

The stacking sequence used was [0/90]<sub>1s</sub> for all laminates.

### 2.3. Moisture absorption test

The water absorption behavior of the composites was investigated as reported by the ASTM D 570-98 standard method [51]. Before water immersion, specimens with 25 × 25 (mm × mm) size, were conditioned by drying in an oven at 50 °C for 24 h and cooled in a desiccator. Afterwards, the samples were immediately weighted by using a 4-digit analytical balance (KERN ABJ 120-4NM) and soaked in water both at room temperature and 50 °C heated for different time points: at the first for 2, 4, 6, 8, 10 and 24 h, then every 24 h until the saturation was achieved. The samples exposed to water were labelled with the names reported in Table 1, followed by RT and 50 °C, respectively. For each time point, samples were taken out and dried with absorbent paper, to remove any surface moisture, and reweighted.

The moisture content percentage,  $M(t)\%$ , was calculated as a difference between the weights of each sample before and after immersion in water for all time points, as in the following equation:

$$M(t)\% = \frac{M_t - M_0}{M_0} \cdot 100 \quad (2)$$

where  $M_0$  and  $M_t$  represent the mass of the sample after conditioning and after exposure to the water, respectively. The testing was carried out until the percentage of water uptake reached equilibrium (daily weight gain of the samples <0.01%) [51,52]. For each test and type of composite, three samples were tested and the average values of the moisture content percentage were reported as a function of the square root of time (hours).

The ability of water molecules to penetrate through laminate composites was evaluated using the diffusion coefficient  $D$  calculated according to ASTM D 5229 standard method [53] as it follows:

$$D = \pi \left( \frac{h}{4 \cdot M_\infty} \right)^2 \cdot \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (3)$$

where  $M_\infty$  is the percentage of humidity absorbed at saturation,  $h$  is the thickness of the sample,  $(M_2 - M_1)$  is the slope of the moisture absorption rate diagram during the initial ageing time,  $(t_2 - t_1)$  is the linear portion of the curve. The weight change should vary linearly with the square root of time, assuming that the absorption process is linear at an early stage of immersion.

In parallel, any loss of matter from the composites during the immersion was evaluated [51]. The specimens after the test were reconditioned in an oven at 50 °C for 24 and after cooling in a desiccator were weighed. The percentage of the soluble matter lost SML% was calculated as follows:

$$SML\% = \frac{M_0 - M_r}{M_0} \cdot 100 \quad (4)$$

where  $M_0$  and  $M_r$  are the weight of the sample after conditioning and after reconditioning, respectively.

### 2.4. Mechanical characterization after water absorption

Specimens for tensile tests with a plate geometry and 25.4 × 254 ×  $t_h$  (mm × mm × mm, with  $t_h$  reported in Table 1) size were cut out from laminates using a diamond wheel saw. All specimens were cut with fabric warp yarns oriented in the axial direction. After that, specimens were soaked in 50 °C heated water for the time needed to reach saturation. This latter was detected by the moisture adsorption test (see Table 2,  $M_\infty$ ). Afterwards, the  $t_h$  of the specimens were measured again and tensile quasi-static tests were performed according to the standard ASTM D 3039/M [28] using an electromechanical testing machine MTS equipped with a load cell of 5 kN. Tests were carried out with a crosshead speed of 2 mm/min at room temperature. An extensometer having a gauge length of 50 mm was used to record the axial deformation during each test. Five samples were tested for each configuration, as defined by Ref. [28]. Load, displacement and strain were acquired during tests by using a sampling frequency of 10 Hz. Stress-strain curves were measured and both Young's moduli and ultimate tensile strengths were derived accordingly. Average values and standard deviations were calculated for each specimen configuration.

### 2.5. SEM microscopy study

A Scanning Electron Microscope (SEM Zeiss SUPRA35, Berlin, Germany) was used before and after the moisture absorption test to observe the morphology of the composites' surfaces and to evaluate if modifications were induced by the water uptake. SEM observations were also carried out after the mechanical tensile tests to observe the fractured surfaces. Before SEM observations, all samples were covered with a thin Au layer to get the good conductivity needed for the

**Table 2 – Saturation time, maximum moisture adsorption and calculated diffusion coefficient for each composite.**

Label	Saturation time, ST [h]		Maximum moisture absorption, $M_\infty$ [%]		Diffusion coefficients, $D$ [m <sup>2</sup> /s]	
	RT	50 °C	RT	50 °C	RT	50 °C
UT	408	168	7.74	9.67	$1.85 \times 10^{-6}$	$5.95 \times 10^{-6}$
N1	528	144	7.86	9.73	$1.85 \times 10^{-6}$	$5.98 \times 10^{-6}$
N5	528	288	6.46	8.19	$1.26 \times 10^{-6}$	$5.57 \times 10^{-6}$
S1	432	264	6.76	8.28	$1.35 \times 10^{-6}$	$5.60 \times 10^{-6}$
S5	528	288	5.58	8.13	$1.21 \times 10^{-6}$	$5.38 \times 10^{-6}$
S20	504	144	7.24	8.45	$1.30 \times 10^{-6}$	$5.81 \times 10^{-6}$

measurements. The acquired images were analyzed by ImageJ software to measure the average diameter of pores.

### 3. Results and discussion

#### 3.1. Moisture absorption test

The ability of the samples in absorbing moisture was evaluated by soaking the samples in water and following their weight growth over time. Fig. 1a–c shows the curves of the adsorbed water percentages at room temperature, whereas Fig. 1d–f shows the curves measured at 50 °C, as a function of the square root of the time (hours) for each composite.

The results obtained for all samples show that the amount of adsorbed water increases with time and that the water uptake is linear and fast at the beginning of the exposition, then slows down until the equilibrium was reached. The achievement of saturation is visible as a plateau in the curves. Therefore, the shape of the curves proved that the moisture adsorption follows a Fickian behavior [54]. Also, the water uptake is affected by both temperature and chemical treatment.

Table 2 reports the saturation time  $S_T$ , the maximum water uptake  $M_\infty$ , recorded for each composite, and the calculated diffusion coefficient  $D$ . The values of  $M_\infty$  and  $D$  also are reported in Fig. 2a and b respectively, to better highlight their trend as a function of the temperature, the reagents used for the chemical treatments and their concentration.

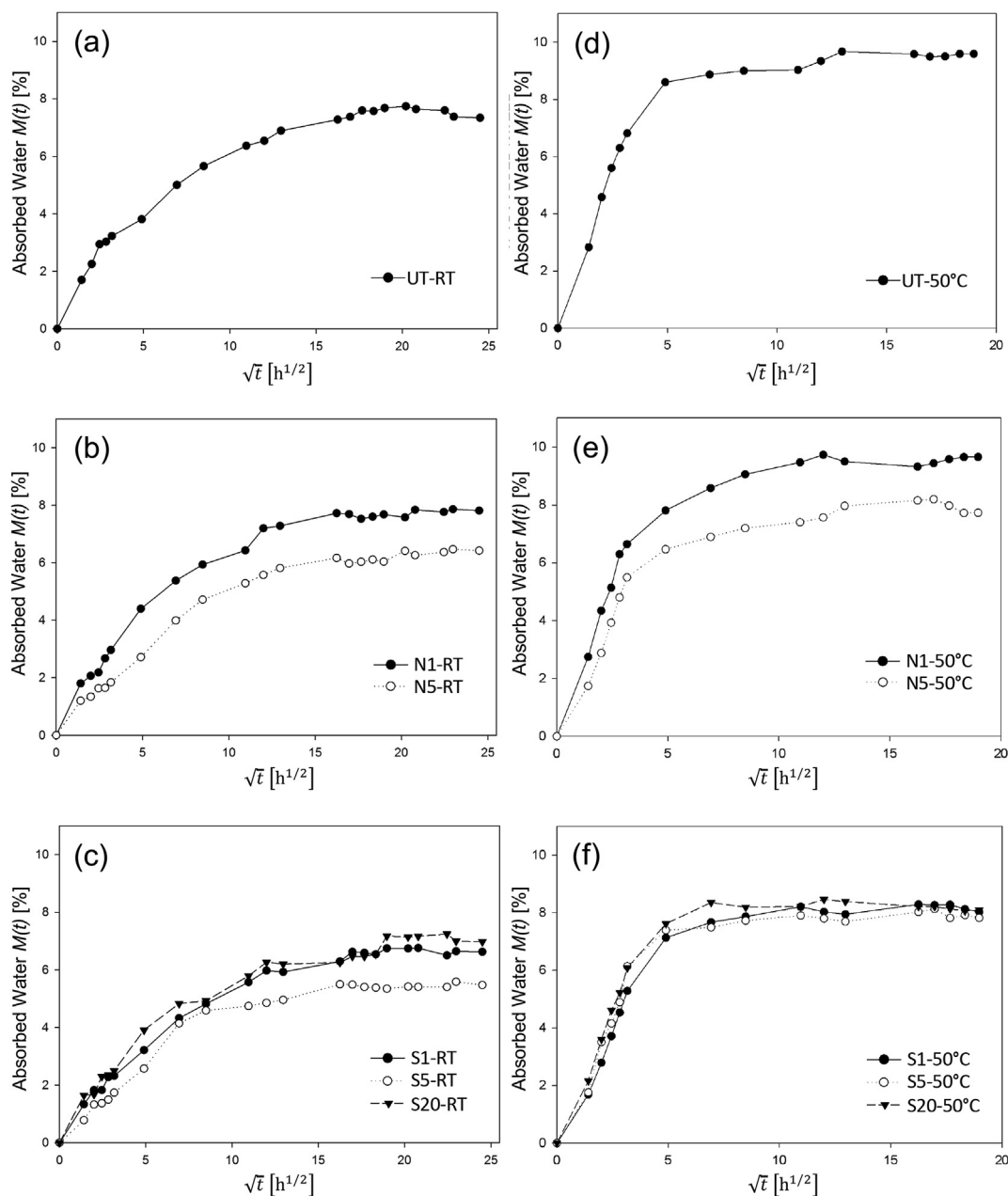
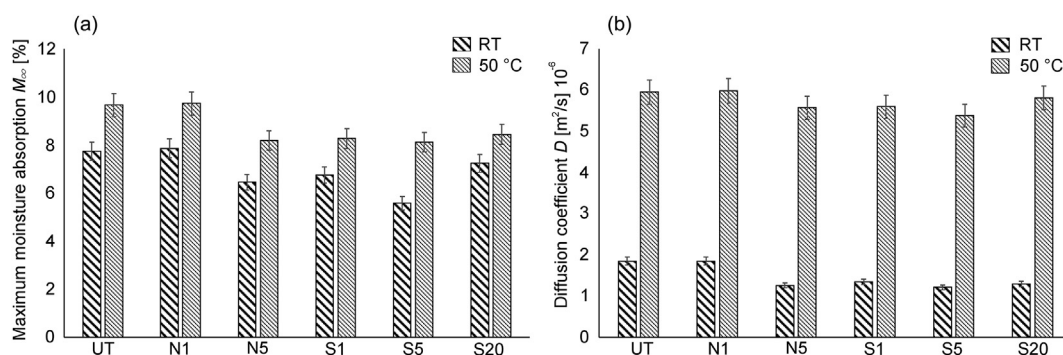


Fig. 1 – Adsorption curves of the specimens soaked in water at room temperature (a, b, c) and heated at 50 °C (d, e, f). On the abscissa, the root of the specimens' dwell time in the water, is expressed in hours.



**Fig. 2 – (a) Maximum moisture absorption,  $M_{\infty}$  in water at room temperature and heated at 50 °C; (b) diffusion coefficients,  $D$ .**

The comparison between the data recorded for the samples soaked in water at room temperature and those exposed to water at 50 °C shows that the higher the temperature, the lower the time to achieve the saturation and the higher the water uptake (see Fig. 2a). In particular, in the case of the composites soaked in water at room temperature, the water uptake reaches the equilibrium between 17 and 22 days (about 408 ÷ 528 h, as shown in Fig. 1a, b and 1c), whereas when the specimens are exposed to 50 °C heated water the saturation is achieved between 6 and 12 days (about 144 ÷ 288 h, as reported in Fig. 1d, c, d). Moreover, in both cases, the lower and the higher maximum moisture uptake were recorded for S5 and N1 composites respectively (Fig. 2a). At room temperature, the maximum amount of water adsorbed was 5.58 for S5 and 7.86 for N1 whereas at 50 °C became 8.13 for S5 and 9.73 for N1. The effect of chemical treatment on the moisture adsorption ability of the composites is affected by both the used reagent and its concentration. All specimens, except N1, show a value of  $M_{\infty}$  lower than UT, proving the efficacy of the chemical treatments. The behavior of N1 is highly different from that one of N5. This proves that the alkali treatment is effective only for suitable concentrations. In the Authors' previous work [33], FTIR analysis showed a decrease in the signals ascribable to the hemicellulose with the increase of the NaOH concentration. Cellulose and Hemicellulose are the hydrophilic components of the fibers [55]. In their structure, indeed, hydroxyl and acetyl groups are present which are the main contributor to moisture adsorption [56]. Therefore, the low uptake of water recorded for the N5 sample can be explained by the decrease of the hygroscopic hemicellulose. The different behavior of N1 is, thus, ascribable to the low concentration of the NaOH solution used to treat the fibers. The process leading to the removal of hemicellulose from the lignocellulose fibers in alkali conditions, indeed, involves the hydrolysis of ester and ether linkages between hemicelluloses and lignin and the removal of acetyl and uronic acid substitutions on hemicellulose [57,58]. When the NaOH concentration is low, only partial removal of the hemicellulose can occur leading to the presence of intermediate species reach of -OH groups on the fibers. This can explain the higher hygroscopicity of N1 composites compared to UT and N5 specimens.

Silane treatments allow obtaining composites with adsorption ability lower than UT. However, only S5 shows a value of  $M_{\infty}$  lower than N5, proving to be the better treatment

for hindering water adsorption in the studied composites. Therefore, also in the case of the silane treatment, the concentration of the coupling agent has an essential role. A concentration lower than 5 wt% (GPTMS 1% solution) probably is not sufficient to improve significantly the linkage between the fibers and the matrix, because only a few -OH groups of the fibers can react with the coupling agent. On the contrary, an excessive concentration of silane (GPTMS 20% solution) could produce an increase of -OH groups on the fibers. When GPTMS is dissolved in the alcohol/water solution, indeed, a sol-gel process starts [59,60] leading to the GPTMS hydrolysis in the first step. Therefore, silanol groups (Si-OH) are formed due to the substitution of the alkoxy groups by hydroxyl groups. Once formed the hydrolysis products, the formation of siloxane bonds (Si-O-Si) takes place due to the condensation reaction between two partially hydrolyzed GPTMS molecules or between a partially hydrolyzed GPTMS molecule and a not hydrolyzed one. The hydrolysis and condensation proceed simultaneously leading to the formation of oligomers. When the fibers are soaked in the solution, the formed oligomers can interact with the fibers by hydrogen bonds involving the -OH groups of the oligomers and those of the lignocellulose fibers. Finally, covalent bonds between the fiber and the coupling agent are formed during the fibers drying treatment [33]. Therefore, when an excess of GPTMS is present, many hydroxyl groups on the fibers can react with the formed oligomers but, at the same time, a higher amount of residue silanol groups will be present due to the high number of oligomers and their incomplete condensation. This could explain the highest water adsorption value recorded for the S20 specimen compared to S1 and S5 samples [49].

Moreover, the results reported in Table 2 and Fig. 2a and b shows that the values of  $M_{\infty}$  are well correlated to the calculated  $D$  values; S5, indeed, shows the lower values of both  $M_{\infty}$  and  $D$ , whereas N1 the higher ones.

The specimens showing the higher and the lower value of  $M_{\infty}$  for each chemical treatment were observed by SEM before and after soaking in water at room temperature and 50 °C heated (see Fig. 3). All specimens, except S5, show the presence of pores on their surface already before the exposure to the wet environment. The average size of the pores varies as a function of the chemical treatment, as shown in Table 3.

Fig. 3a (UT specimen) shows the biggest pores (average size 100  $\mu\text{m}$ ) whereas S5 (Fig. 3l) is the only sample without any pores before soaking. Results suggest that pores' presence and

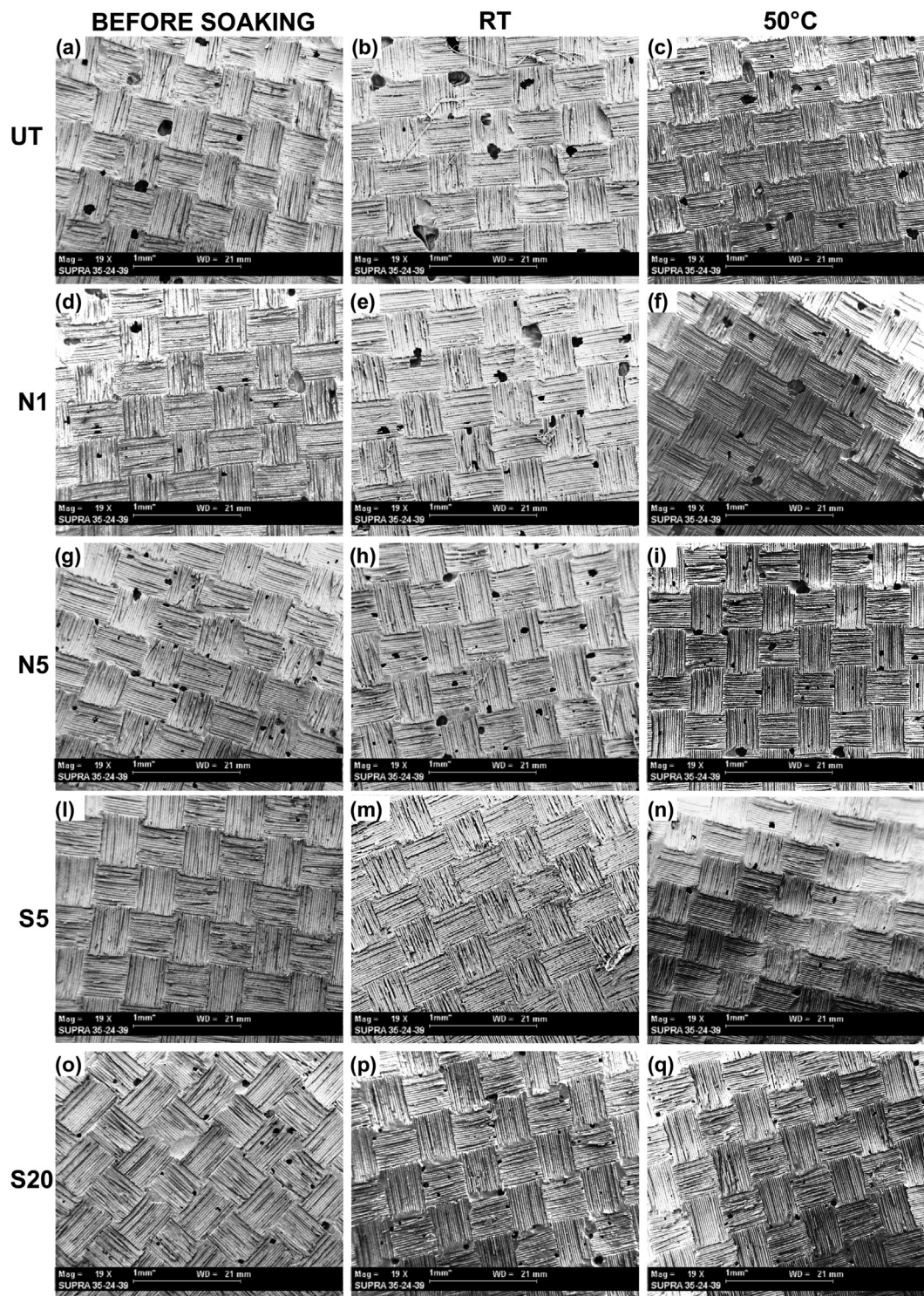


Fig. 3 – SEM micrographs of the samples before and after the adsorption test.

size contribute to the water adsorption but, at the same time, reflect the strength of the linkage between the fibers and the matrix. After soaking in water at room temperature, only a slight broadening of the average size of the pores was observed. This phenomenon is more evident in the sample UT, reported in Fig. 3b. UT (Fig. 3b) is also the only sample for which the loss of soluble matter was recorded at room

temperature (Table 3). Therefore, probably the observed pore broadening is due to the detachment of resin fragments. The increase of water temperature up to 50 °C, leads to the increase of both the number of pores (Fig. 3) and the loss of soluble matter (Table 3) for all samples.

The average pore size, instead, decreases probably due to the formation of new pores. The effect of the temperature is

**Table 3 – Soluble matter lost percentages calculated after reconditioning and average pores size.**

Label	Soluble Matter Lost SML [%]		Average pore size [μm]		
	RT	50 °C	Before soaking		
			RT	50 °C	50 °C
UT	0.03	0.04	100	139	90
N1	<0.01	0.12	65	78	80
N5	<0.01	0.29	66	74	80
S5	<0.01	0.26	0	0	58
S20	<0.01	0.11	63	61	52

less evident for UT and N1 specimens (Fig. 3c–f), which indeed show the lowest SML, whereas is more evident for S5 (Fig. 3n), where the formation of pores takes place and the highest SML was recorded. The increase of sample porosity after soaking in 50 °C heated water contributes to explaining the higher water uptake of such samples compared to those soaked at room temperature.

**3.2. Tensile testing**

After the moisture adsorption test, the exposed to 50 °C heated water specimens, which were the samples adsorbing the highest amount of water, were subjected to quasi-static tests. Applied loads, crosshead displacements and strains were acquired during tests to generate stress-strain curves, ultimate tensile strength values and Young’s moduli of the different specimen configurations.

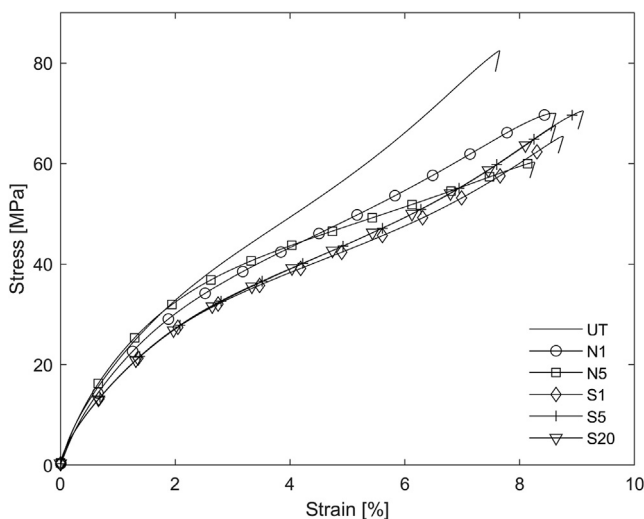
Stress-strain curves measured after the moisture absorption tests for the laminates manufactured with the treated fibers were reported in Fig. 4. All curves display a small linear range within nearly 1%, followed by a hardening region that continues up to failure, occurring between 7 and 9% depending on the chemical treatment made on the fibers.

The elongation at break of the specimens prepared with chemically treated fibers is higher than that of the UT one.

However, the ultimate tensile strength (i.e. the peak values for stresses) of composites reinforced with chemically treated fibers is lower than that of composites reinforced with untreated fibers (Fig. 5). The UT specimen presents an ultimate tensile strength of 83.2 MPa, whereas N1 and N5 presented ultimate stresses of 70.2 MPa and 60.2 MPa respectively. Fibers treated with solutions of silane presented alternating performances depending on the Silane concentration, with the highest values (71.3 MPa) observed for the 5% concentration. Young’s moduli reported in Fig. 6 were calculated starting from the stress-strain curves using the secant method, according to the standard [28]. Young’s moduli values of N1 and N5 are similar to that measured for UT, whereas silane-treated fibre-based composites show lower values.

To evaluate the modification of the mechanical performances of each specimen configuration induced by water adsorption and, thus, explain the obtained results, it is essential to distinguish the effects ascribable to the fibers chemical treatments from those due to the water uptake. For this purpose, the data obtained in the present work were compared with the results reported in the previous one [33] (see Figs. 7 and 8), where specimens were tested similarly even though not exposed to a moisture environment. Moreover, it was possible to evaluate the effectiveness of the chemical treatments in the prevention of the composites’ mechanical failure induced by moisture adsorption.

The trend of both elongation and the ultimate tensile strength as a function of the chemical treatment is almost in agreement with the results obtained with tests without moisture-exposed specimens by Sepe et al. [33] previously. The Authors ascribed the reduction of the tensile strength to the removal of hemicellulose and lignin induced by the chemical treatments and observed by FTIR analysis carried out on fibers after the chemical treatments. When hemicellulose and lignin were removed from the treated fibers, indeed, cellulose microfibrils received less support against tensile loading [43]. Such structural modification was more evident after alkali treatment, and in particular, after treatment with 5% NaOH



**Fig. 4 – Tensile stress-strain curves for different chemical treatments after immersion at 50 °C.**



which caused a fibrillation phenomenon, as observed by SEM [33]. Moreover, the higher thickness of laminates made with the alkali-treated fibers, compared to that one of the laminates made with silane-treated fibers (see Table 1), also contributes to explaining the higher observed strength lowering. The removal of hemicellulose and lignin covering cellulose fibrils, also leads to an easier slippage. Therefore, the UT, where hemicellulose and lignin between the cellulose microfibrils held the microfibrils in position and resisted slippage to an extent, had greater resistance against tensile loading and lower failure strain than NaOH treated-fibre composites [43]. On the contrary, the laminates containing 1% and 5% silane-treated fibers showed lower failure strength than those untreated due to both the low structural modification of the fiber caused by the chemical treatment and the higher stiffness due to the better fibers-matrix interface [33].

After the moisture adsorption test, the values of the elongation at break increase further due to the further

destructuring of the fibers caused by the absorbed water. Water molecules, indeed, form H-bonds with the OH-groups of the cellulose microfibrils leading to the rupture of the bonds among them [61]. Moreover, water molecules bonded to cellulose cause the formation of a slippery layer which reduces the frictional resistance between microfibrils during the tensile deformation of the fibers [43]. These phenomena result in easy deformations of cellulose microfibrils during tensile loading and fiber swelling [43,61]. On the other hand, despite the thickness increase of all laminate (see Table 4), the ultimate tensile strength values after the moisture adsorption test change significantly only for S1 and S20 (see Fig. 7).

The thickness of the silane-treated fiber-based composites, indeed, shows a percentage increase of swelling higher than the other specimen configurations after water adsorption. This observation contributes to explaining the highest ultimate tensile strength lowering of S1 and S20. However, it is

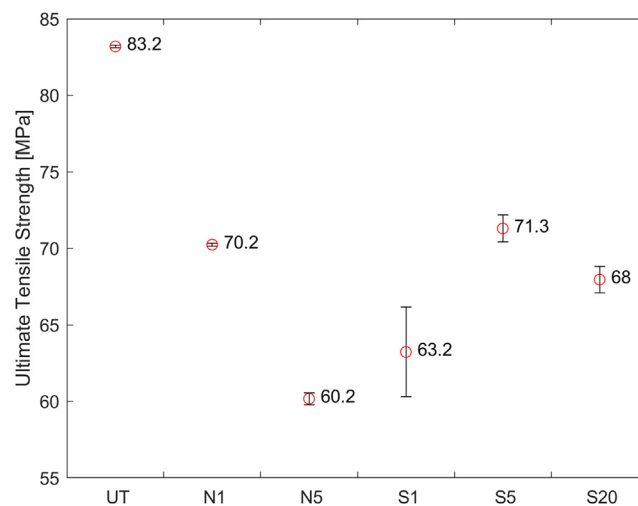


Fig. 5 – Ultimate tensile strength of the treated fiber composites after immersion at 50 °C.

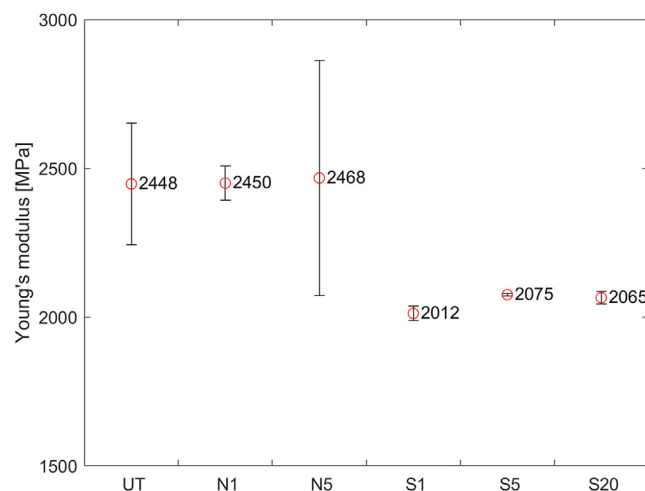


Fig. 6 – Young's modulus of the treated and untreated fiber composites after immersion at 50 °C.

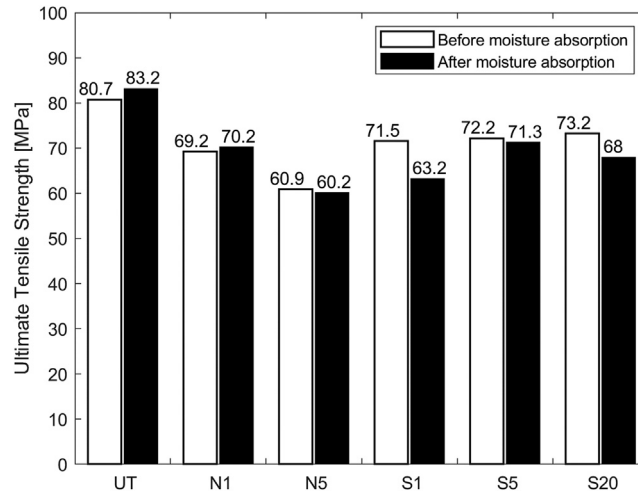


Fig. 7 – Ultimate tensile stresses of the treated fiber composites before and after immersion at 50 °C.

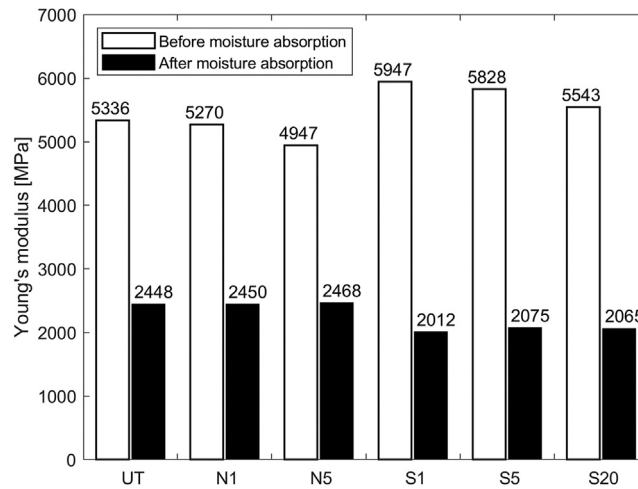


Fig. 8 – Young's modulus of the treated fiber composites before and after immersion at 50 °C.

Table 4 – Comparison between tensile properties of the composites before and after immersion at 50 °C. The data recorded before the moisture adsorption test are referred to in the previous work [33].

Label	$T_h$ [mm]		Ultimate tensile Strength [MPa]		Young's modulus [MPa]	
	Before water adsorption	After water adsorption	Before water adsorption	After water adsorption	Before water adsorption	After water adsorption
UT	1.36	1.47	80.7	83.2	5336	2448
N1	1.51	1.63	69.2	70.2	5270	2450
N5	1.68	1.75	60.9	60.2	4947	2468
S1	1.47	1.65	71.5	63.2	5947	2012
S5	1.46	1.64	72.2	71.3	5828	2075
S20	1.45	1.63	73.2	68.0	5543	2065

noteworthy that S5 is not subjected to this strength lowering. Therefore, the high thickness increase is not the unique reason for the strength reduction of S1 and S20. According to the moisture adsorption data, S1 and S20 show a water uptake higher than S5. Therefore, the fibers, as well as the fiber-

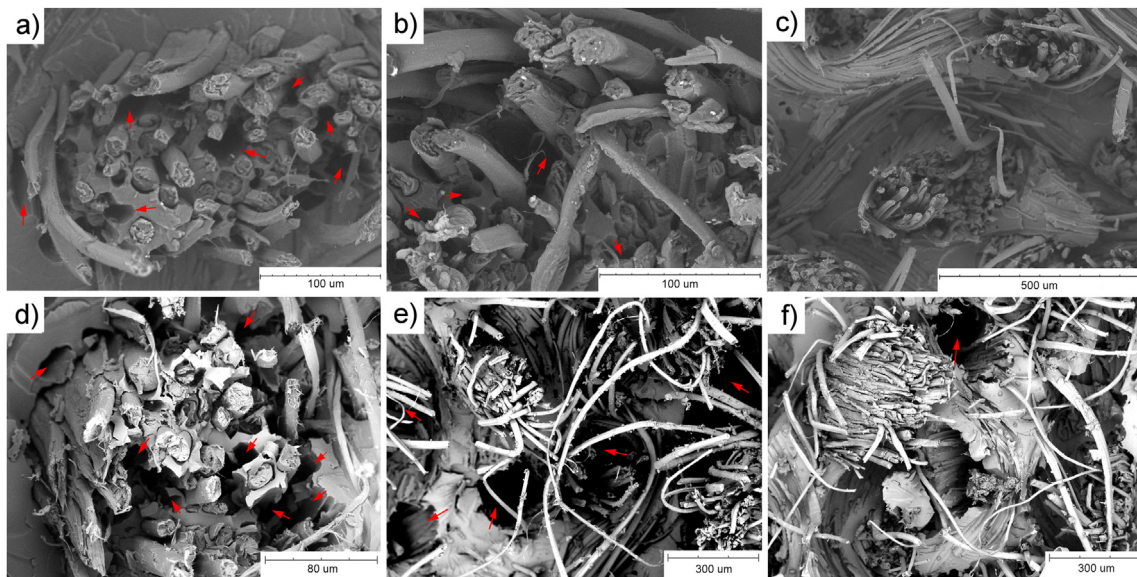
matrix interface, undergo more damage due to absorbed water. The free water, indeed, damages fiber structure leading to their swelling which, in turn, results in the development of shear stress at the fiber-matrix interface, leading to the ultimate debonding of the fibers, delamination, loss of structural

integrity and decreased in mechanical properties [62]. This behavior also was confirmed by SEM analyses. Fig. 9a and d shows the SEM micrographs of the tensile fractured surface of N5 specimens before and after immersion in 50 °C heated water. The presence of cavities or gaps around fibers can be observed clearly both before and after soaking in 50 °C heated water. This indicates the poor adhesion between hemp fibers and matrix. Therefore, when stress is applied it causes the fibers to be easily pull-out from the matrix (red arrow), leaving behind gaping holes. For this reason, there is no difference in tensile strengths recorded before and after immersion. The fracture surfaces of silane-treated composite S1, before and after immersion in 50 °C heated water, are shown in Fig. 9b and e. The presence of resin embedded on the surface of fibers, before immersion, can be observed in Fig. 9b indicating better interfacial adhesion between fiber-matrix. This confirms the high strength of the laminate treated with silane. In addition, after silane treatment also a reduction of holes due

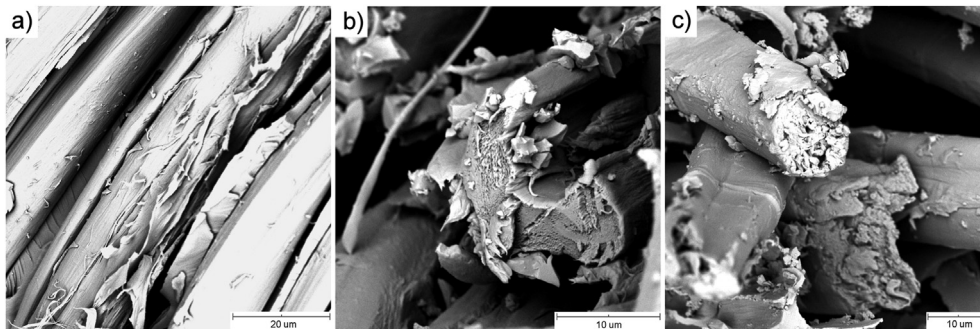
to fiber pull-out is observed (Fig. 9b) compared to alkali treatment (Fig. 9a). After immersion of S1 composite the number of holes due to fiber pull-out increases (Fig. 9e) due to the water uptake that swells the fibers resulting in the development of shear stress at the fiber-matrix interface which, in turn, leads to the debonding of the fibers, and loss of structural integrity.

Fig. 9c and f shows the fracture surfaces of S5 specimens before and after immersion at 50 °C. Before the immersion, there is no presence of holes due to pull-out (Fig. 9c) and this explains the higher strength of the S5 composite than S1. After the immersion, the good adhesion between fiber and resin continues (Fig. 9e) and thus no loss of tensile strength is recorded for the S5 composite.

The damage to the fiber structure and mainly to the fiber-matrix interface causes also the dramatic reduction of Young's moduli measured for all the laminates after the moisture adsorption test. This result is in agreement with



**Fig. 9** – SEM images of surface fracture of specimens: (a) N5 before immersion; (b) S1 before immersion; (c) S5 before immersion; (d) N5 after immersion at 50 °C; (e) S1 after immersion at 50 °C; (f) S5 after immersion at 50 °C.



**Fig. 10** – Fiber morphology after the fracturing of specimens: (a) N5 after immersion at 50 °C; (b) S1 after immersion at 50 °C; (c) S5 after immersion at 50 °C.

several works in the literature [17,62,63]. This lowering is about 50% for UT and alkali-treated fiber composites whereas it is more extended for the specimens containing silane-treated fibers (about 60%) (see Fig. 8). Before the moisture adsorption test, silane-treated fiber composites showed the highest value of Young's moduli, proving the effectiveness of silane treatment in the improvement of the compatibility and adhesion between the hemp fibers and the epoxy matrix [33]. Both the negative effect of water on adhesion between fiber and matrix and the damage of the matrix explain the reduction of Young's moduli in all samples. Its extended effect in the silane-treated fiber composites could be due to both the higher fiber structure modifications induced by absorbed water and the damage of the fiber-matrix interface. The better interfacial adhesion between the fibers and the matrix is proved also by the presence of some pieces of the matrix still bonded to the fibers after they are pulled out from the resin as shown in Fig. 10b and c. The structure of alkali-treated fiber composites, instead, was already damaged before water uptake [33] and after immersion, this damage is improved (Fig. 10a).

Therefore, the obtained results prove that after water uptake all laminates exhibit lower stiffness but still provide the same loading capabilities.

#### 4. Conclusions

An experimental campaign was conducted to quantify the effects of water absorption on the properties of Natural Fibers Reinforced Composites (NFRC) manufactured with hemp fibers chemically treated using NaOH and silane (GPTMS) solutions with different concentrations. The prepared laminates were subjected to a moisture adsorption test to evaluate the effect of chemical treatment on the water uptake ability of the composite. Afterwards, tensile strengths and elastic moduli of composites were evaluated through experimental tests and the results were compared with those previously obtained [33] on specimens prepared similarly but not subjected to a wet environment.

The results show that the effect of the chemical treatments depends on both the used reagents and their concentration. In particular, the 5% NaOH (N5) and 5% silane (S5) treatments led to the lowest water adsorption (6.46 and 5.58% at room temperature and 8.19 and 8.13% at 50 °C, respectively). The higher the temperature, the higher the water uptake, regardless of the chemical treatment, perhaps due to the formation of pores in the matrix, as proved by both SEM observation and the detection of soluble matter lost only after heating. Results of mechanical tests showed that wetted and non-wetted NFRC specimens had approximately the same loading capabilities as proved by the comparison between their ultimate tensile stress values. At the same time, the water adsorption led to a stiffness decrease due to the damage to both the fibers structure and fiber-matrix interface. This reduction was lower for the S5 specimen, proving that the 5% silane treatment was the best choice for hindering the water adsorption and the entailed failure of the composites.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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