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The Natural Growth of $CaCO_3$ Crystals on Hemp Yarns: A Morphology Analysis and the Mechanical Effects on Composites

Quentin Drouhet, Romain Barbière, Fabienne Touchard *, Laurence Chocinski-Arnault and David Mellier

Department of Physics and Mechanics of Materials, Pprime Institute, CNRS-ENSMA-University of Poitiers, ISAE-ENSMA 1 Avenue Clément Ader, 86961 Futuroscope Chasseneuil, France; quentin.drouhet@ensma.fr (Q.D.); romainbarbiere95@gmail.com (R.B.); laurence.chocinski@ensma.fr (L.C.-A.); david.mellier@ensma.fr (D.M.)
* Correspondence: fabienne.touchard@ensma.fr

Abstract: Plant fibres are promising candidates to replace synthetic fibres in polymer matrix composites. However, there is still an important issue to overcome: the poor quality of adhesion at the fibre/matrix interface. Many surface treatments of plant fibres have been developed, most of them based on non-environmentally friendly processes. In this paper, a 100% natural treatment is proposed. Hemp yarns are immersed in tap water until the natural growth of limestone beads attached to their surface occurs. The morphology analysis reveals that these calcium carbonate crystals have a nanoneedle architecture, with hemp fibres acting as nucleators for these highly ordered coral-like structures. Tensile tests on $\pm 45^{\circ}$ woven hemp/epoxy composites show that the presence of $CaCO_3$ beads improves the adhesion quality of the fibre/matrix interface and, therefore, increases Young's modulus value.

Keywords: natural fibres; fibre/matrix bond; surface treatment

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1. Introduction

With increasing economic and environmental concerns, synthetic fibres tend to be replaced in composites by reinforcements of plant origin, which have good specific properties compared to glass fibres [1–4]. The most common plant fibres used in biocomposites are hemp, flax, sisal and jute [5]. Numerous methods have been developed for manufacturing bio-composites, depending on the targeted application: hand lay-up technique, compression moulding, vacuum infusion, pultrusion, etc. [6]. Interest in biocomposites is growing rapidly in the automotive, aerospace, marine and construction industries [7]. In the present study, continuous hemp reinforcement is used. Hemp (*Cannabis sativa* L.) cultivation allows for the diversification of crop rotations and requires little herbicides and fertiliser. Hemp is one of the oldest crops and is now considered one of the most environmentally friendly industrial fibres [8–10]. Hemp bast fibres have long been used in textile production because they are particularly long and contain highly crystalline cellulose fibrils [11]. However, as for other plant fibres, the optimisation of the interfacial bonding between the plant reinforcement and the polymer matrix is one of the most essential procedures for the optimal formulation of hemp composites. Modification of the plant fibre surface is necessary to produce a composite with enhanced interfacial bonding and efficient stress transfer at the interface [12]. Various methods have been explored to improve the compatibility and adhesion between lignocellulosic molecules and hydrocarbon-based polymers [13]. The most common chemical processes are based on permanganates, liquid ammonia or isocyanate treatments or consist of silane coupling, esterification and graft copolymerisation [14–16]. Enzymatic treatments have also been tested for different types of plant fibres [17]. The physical methods commonly used are corona, heat treatment, electric

discharge or plasma treatment [18,19]. But all these treatments are not environmentally friendly because they require the use of chemicals and/or energy-consuming equipment.

In this paper, a 100% natural treatment is proposed. A morphology investigation of the hemp yarn surface is performed using optical and scanning electron microscopy. Previously unseen images of limestone beads attached to hemp fibres were obtained. Tensile tests are then carried out on ±45° woven hemp/epoxy composites made with untreated or treated hemp fabric.

2. Materials and Methods

2.1. Materials

Hemp yarns were provided by *Lin et L'autre* (Château d'Oléron, France). They were made of bundles of hemp fibres twisted together with a mean twisting angle of around 11° and a linear density of about 83 tex, as determined in a previous study [20]. Single yarn tensile tests were performed according to ASTM C-1557 [21]. Individual hemp yarns were glued onto card tabs with a central window cut out to obtain a gauge length equal to 10 mm (Figure 1a).

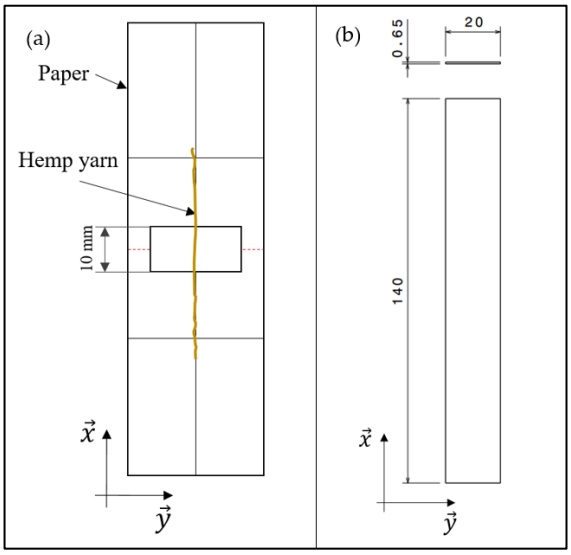


Figure 1. Geometry of the samples for tensile testing (in mm). (**a**) Single hemp yarn samples. (**b**) Woven hemp composites.

Composites were made of a single plain-woven layer of hemp fabric with an areal density of 290 ± 10 g/m^2. Composite plates with treated or untreated hemp fabric were manufactured by vacuum infusion. The principle of this technique is to infuse resin into the laminate. The first step is to place the hemp fabric in the mould. Next, a perforated release film is positioned over the dry reinforcement. A vacuum is applied, and the dry fabric is compacted. Still under vacuum, the resin is infused into the mould to impregnate the hemp fabric. The resin used was the EPOLAM 2020 epoxy from *Axson* (Cergy, France). After manufacturing, composite plates were cured with the following cycle to achieve a cross-linkage as complete as possible: 24 h at ambient temperature, 3 h at 40 °C, 2 h at 60 °C, 2 h at 80 °C and 4 h at 100 °C. Rectangular samples were cut from composite plates to obtain ±45° reinforcement orientation. Overall dimensions of samples were 140 mm in length, 20 mm in width and 0.65 mm in thickness (Figure 1b).

2.2. Surface Treatment

A crucial issue with plant fibre composites is their durability when they are subjected to the presence of moisture. Indeed, plant fibres are highly hydrophilic in comparison with the polymer matrix. When a plant fibre composite is exposed to water ageing, its sensitivity to moisture leads to a decrease in the adhesion quality at fibre/matrix interface and to

the degradation of its mechanical properties [22–24]. As part of our work to analyse the damage mechanisms occurring during water ageing, hemp yarns were immersed in tap water at room temperature. The hardness of the used tap water was measured to be equal to about 20°f. Some of the hemp yarns were left in water during the whole summer. After three months and the complete evaporation of water, the hemp yarns looked different, as if they had been subjected to a surface treatment. It has thus been decided to conduct an in-depth analysis of the consequences of this 100% natural treatment.

2.3. Differential Scanning Calorimetry

The matrix glass transition temperature (T_g) was determined by modulated differential scanning calorimetry (M-DSC) using Q20 *TA Instruments* (New Castle, DE, USA) device. With conventional DSC, the glass transition can be hidden by an endothermic peak due to the presence of water in samples [25]. By using M-DSC, it is possible to separate reversing and non-reversing heat flows. The reversing heat flow contains thermodynamic components such as glass transition, allowing the determination of the T_g value. Two aluminium pans were used; the first one was empty and used as reference, while the second one was filled with the composite sample (mass of material was between 5 mg and 10 mg). The method used was as follows: equilibrate at 0 °C; modulate ± 0.796 °C every 30 s; ramp 10 °C/min to 180 °C. The modulation amplitude was chosen according to the modulation period and the heating rate in order to detect the glass transition temperature more easily.

2.4. Microscopic Observations

A morphological investigation of the treated and untreated hemp yarns was carried out using a *ZEISS* (White Plains, NY, USA) Axio Imager optical microscope and a *JEOL* (Peabody, MA, USA) JSM-7000F field emission gun scanning electron microscope (FE-SEM). Prior to FE-SEM observations, specimens were sputter-coated with gold.

2.5. Tensile Testing

Tensile tests on individual hemp yarns were carried out at room temperature with an *Instron* (Norwood, MA, USA) 1195 machine equipped with a 500 N load cell. Tests were performed in displacement control with a crosshead speed of 0.1 mm/min. The apparent strain was determined from the crosshead displacement.

Tensile tests were carried out on composite samples using an *Instron* 5982 tensile testing machine with a crosshead speed of 0.5 mm/min. Longitudinal strain was measured by a 12.5 mm gauge length extensometer.

3. Results and Discussion

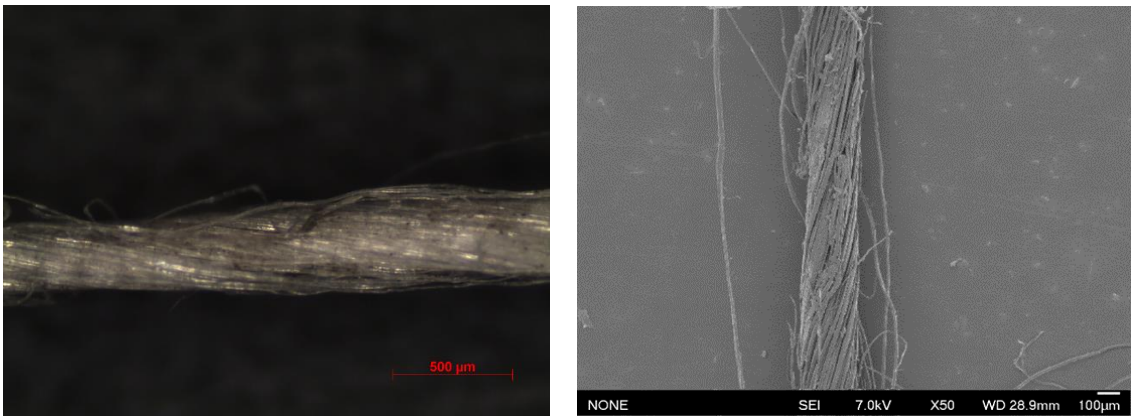
3.1. Morphology Analysis of $CaCO_3$ Crystals

The morphological investigations were performed by optical microscopy and SEM observations. Representative images of the untreated hemp yarns are presented in Figure 2. Observations show the bundles of hemp fibres twisted together to form the yarn. Each individual hemp fibre has a diameter of about 13 µm. It is also possible to see that hemp fibres are bonded together with lignin and waxy substances and that there are some impurities (Figure 2b).

After three months of water ageing, the hemp yarns became rough to the touch. Their observations by optical microscopy revealed the presence of small beads (Figure 3). These beads are globally spherical, spread all along the yarns and sometimes imbricated in each other. Their diameter can vary from 100 µm to 500 µm. They are well attached to the yarns: it is difficult to remove them with the fingers. They look like limestone particles, as the ones obtained, for example, by Vidallon et al., who used a precipitation technique based on bovine serum albumin and polydopamine [26]. They obtained particles dispersed in a solution for biomedicine applications.

In order to check that the beads observed in Figure 3 are made of calcium carbonate ($CaCO_3$), a few drops of hydrochloric acid were poured over a piece of treated hemp yarn.

An instantaneous chemical reaction was observed, with the formation of many bubbles, causing the disappearance of the beads and thus confirming that the long ageing in tap water had created limestone beads on the surface of the hemp yarn. To go further in their morphological analysis, SEM observations were also performed (Figure 4).



(**a**) (**b**)

Figure 2. Untreated hemp yarns observed by (**a**) optical microscopy and (**b**) scanning electron microscopy.

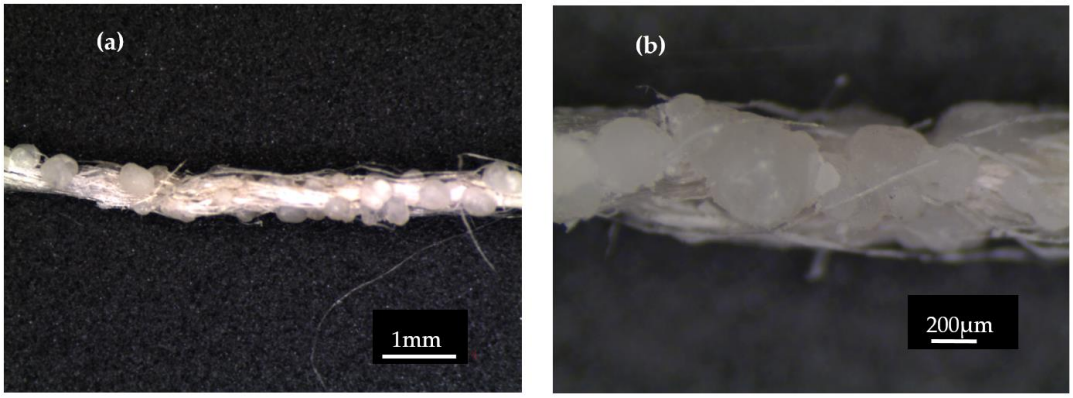


Figure 3. Treated hemp yarns observed by optical microscopy at two different magnifications: (**a**) ×20; (**b**) ×50.

Thanks to high-magnification images, it is possible to see that the beads are, in fact, crystals with a nanoneedle architecture (Figure 4d). The hemp fibres act as nucleators (Figure 4c), leading to a strong connection of the beads to the hemp yarn (Figure 4b). To the best of the authors' knowledge, such images of $CaCO_3$ beads fixed onto natural fibres have never been shown before. This well-aligned architecture reminds us of a highly ordered coral-like structure. The long ageing of hemp yarns in tap water led to biomineralisation-like effects. Indeed, the biomineralisation process leads to the creation of self-organised structures, such as coral, sea shells and coccoliths [27]. $CaCO_3$ is abundant as a biomineral in nature. Some research groups work to reproduce biomineralisation by developing controlled processes, allowing for the selection of the design of the obtained biominerals. These studies belong, in particular, to the fields of biomedicine [28–31] or papermaking [32,33]. P. Alam et al. studied the effect of a $CaCO_3$ coating on the mechanical behaviour of flax fibres [34–36]. They soaked the flax fibres in an acetic acid solution containing ground calcium carbonate in order to create a thick mineralised cake enveloping the fibre surface. They demonstrated that this exoskeleton enhances the mechanical properties of the flax fibres. The current study utilises a completely natural method (immersion in tap water) to achieve mineralisation, which leads to the formation of small beads of $CaCO_3$ instead of a dense exoskeleton.

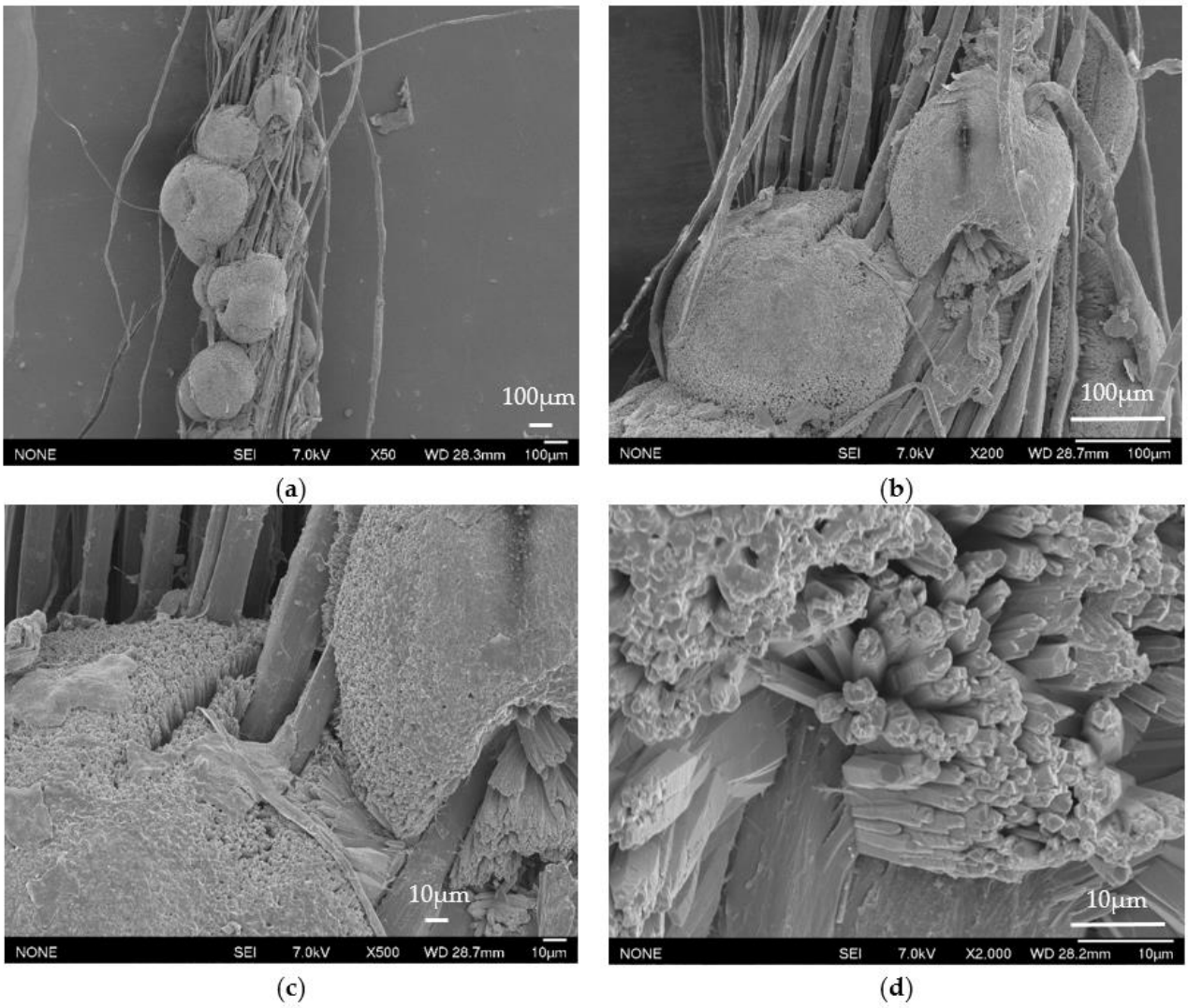


Figure 4. (**a**–**d**) Treated hemp yarns observed by SEM.

3.2. Tensile Tests on Treated and Untreated Hemp Yarns

Tensile tests were performed on both treated and untreated hemp yarns. A single hemp yarn sample is shown in Figure 5a. Figure 5b shows examples of curves obtained for treated and untreated yarns.

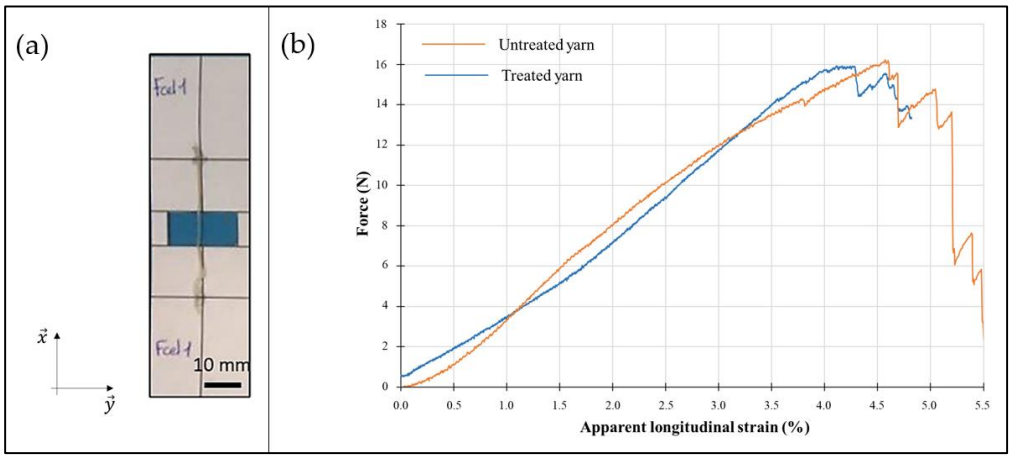


Figure 5. (**a**) Hemp yarn sample. (**b**) Examples of tensile curves for untreated and treated hemp yarns.

Due to their natural origin, hemp yarns exhibit a high variability in their mechanical behaviour. However, these first results obtained on yarns with limestone beads seem to indicate that the applied treatment does not alter the tensile behaviour of hemp yarns (Figure 5b).

The presence of $CaCO_3$ beads with a strong connection to the yarns could be a great opportunity to improve the quality of adhesion at the fibre/matrix interface in woven hemp/epoxy composites. With the aim of checking this possibility, the tap water ageing conditions were reproduced on hemp fabric.

3.3. Characterisation of Composite Plates

The fibre volume fraction V_f of the composite plates was determined thanks to Equation (1):

$$v_f = 1 - \frac{1}{\rho_m}\left(\rho_m - \frac{N_f w_f}{h_c}\right) \quad (1)$$

where ρ_m is the density of the composite matrix, N_f is the number of layers, which is equal to 1 in our case, w_f is the fabric areal density, and h_c is the composite thickness. The obtained V_f value for single-layer hemp/epoxy composites made of treated or untreated hemp fabric was 36.9 ± 2.7%.

Glass transition temperatures of composite plates were determined using the M-DSC technique. An example of reversing heat flow versus temperature curve obtained for a single-layer hemp/epoxy sample is presented in Figure 6. Results produced an average T_g value of 83 ± 1 °C for all the tested composite samples.

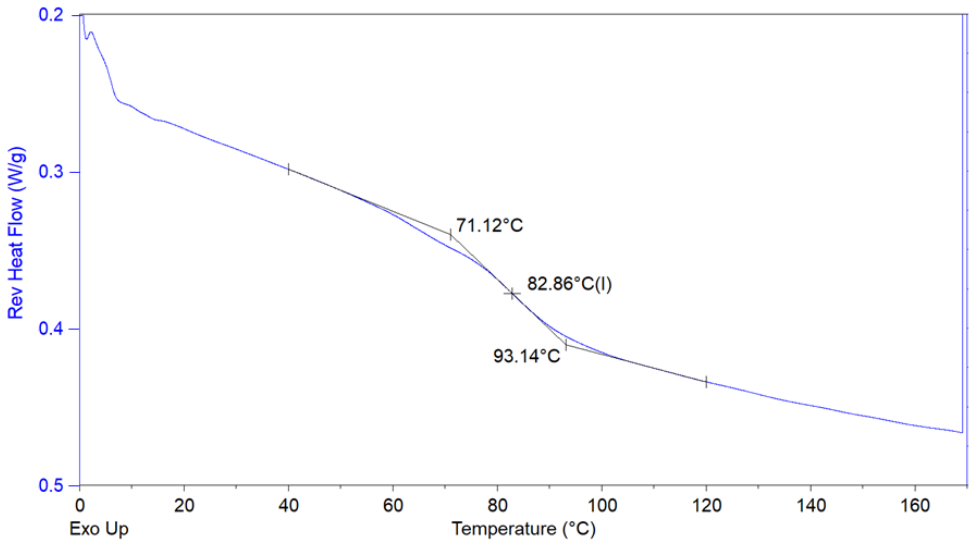


Figure 6. Reversing heat flow from M-DSC thermogram of a hemp/epoxy composite sample.

3.4. Mechanical Comparison of Treated and Untreated Hemp Fabric/Epoxy Composites

In order to investigate the influence of the treatment on the mechanical properties of hemp/epoxy composites, composite plates were made from one layer of untreated or treated hemp fabric and epoxy matrix. Then, ±45° samples were cut from these plates (Figure 7a). This orientation emphasises shear stresses, especially at interfaces, allowing the testing of the quality of adhesion between hemp yarns and epoxy matrix. Three tests were performed for each configuration. It was checked that the specimens broke in the gauge length of the samples (Figure 7a). Figure 7b shows a comparison between examples of tensile curves of ±45° hemp/epoxy samples with treated and untreated fabrics.

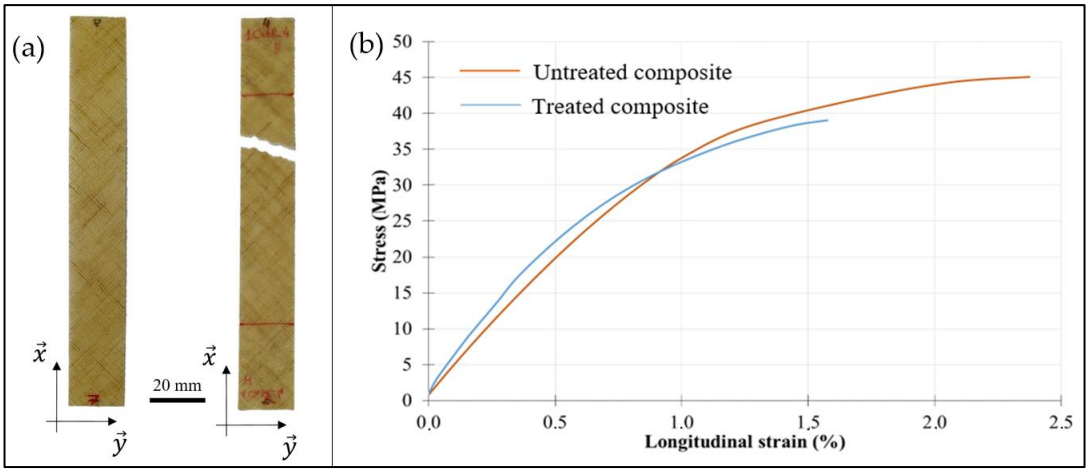


Figure 7. (**a**) Example of a hemp composite sample before and after failure. (**b**) Comparison of representative stress–strain curves for single-layer ±45° composites made of epoxy resin and untreated and treated hemp fabrics.

Results show a decrease in ultimate stress and strain for the treated composite in comparison with the untreated one. The average measured values are summarised in Table 1. The ultimate stress is reduced from 45.0 ± 2.3 MPa to 37.8 ± 1.9 MPa for the untreated composite and the treated one, respectively, representing a decrease of 16%. Concerning the ultimate strain, the drop reaches 32%, from 2.5 ± 0.2% for the untreated composite to 1.7 ± 0.1% for the treated one. This early failure of the treated composite is probably due to the hemp fabric degradation during the water ageing. Results nonetheless show an increase in Young's modulus value. Indeed, Young's modulus value is 14.4% higher for the treated composite than for the untreated one (Table 1). It demonstrates that the treated hemp fabric has a better adhesion with the composite matrix thanks to the presence of the $CaCO_3$ beads. However, scaling up the water ageing conditions from yarn to fabric is complex and requires an adaptation of the treatment process. The conditions must be optimised to achieve enhanced interfacial adhesion while avoiding premature breakage.

Table 1. Comparison of treated and untreated ±45° hemp/epoxy composites.

	Young's Modulus (MPa)	Ultimate Stress (MPa)	Ultimate Strain (%)
Composite with untreated hemp fabric	4240 ± 200	45.0 ± 2.3	2.5 ± 0.2
Composite with treated hemp fabric	4850 ± 200	37.8 ± 1.9	1.7 ± 0.1

4. Conclusions

This study showed how three months of ageing in tap water can produce the natural growth of limestone beads on the hemp yarn surface. A morphology analysis by optical and scanning electron microscopy revealed for the first time that $CaCO_3$ beads were very well attached to the hemp fibres, thanks to many nanoneedles. These calcium carbonate crystals are coral-like structures with a highly ordered architecture. Tensile tests on individual yarns were performed, showing similar behaviours before and after treatment. Tensile tests were then carried out on single-layer woven hemp/epoxy composites made with untreated or treated (i.e., aged in tap water) hemp fabric. Results showed that the ageing in tap water leads to a decrease in the ultimate stress and strain values but an increase in Young's modulus value by 14.4%. This is a very promising result, showing that the presence of $CaCO_3$ beads on hemp yarns allows for the enhancement of the quality of adhesion at the yarn/matrix interface in woven composites. However, it is still necessary to optimise the

scale change of the processing in order to obtain better fabric-scale properties. Furthermore, work is underway to conduct fragmentation tests on monofilament composites with treated hemp yarns to quantify the quality of the adherence at the yarn/matrix interface. Finally, tests on laminates composed of multiple layers of hemp fabric are also being considered. With only a natural and low-cost treatment, these materials could further compete with synthetic glass fibre composites. This opens the door to the development of more efficient biocomposites that could be of interest to industry.

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Conflicts of Interest: The authors declare no conflict of interest.

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